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Theory of the Work Function
II. The Surface Double Layer

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An expression for the work function of a monovalent metal, previously obtained by E. Wigner and the author, included a term which represents the energy required to move an electron through an electrostatic double layer at the surface of the metal. In order to determine the moment of this double layer, it is necessary to make an explicit calculation of the electronic charge density at the surface of the metal, which is attempted in the present paper. In the model taken for this calculation, the density of positive electricity is assumed constant on the negative side of the *YZ* plane, and is zero in the positive half-space. The electrons are so distributed as to neutralize the positive charge density in the interior, and the metal as a whole is neutral. An approximate self-consistent solution of the Fock equations gives the charge density at the surface. An attempt is made to go beyond these equations, so as to include the effect of correlation (or polarization) forces on the double layer. The density of positive electricity assumed is the same as that which would exist in Na if the ions were treated as a continuous charge distribution. The final values obtained are 2.35 and 2.0 ev for the work function, and 0.4 and 1.0 ev for the moment of the double layer, where the first values in each are obtained when the correlation forces are included, and the second when these forces are omitted in the calculation. A comparison of these values with the experimental values of the work function of Na is given. It is concluded that the surface barrier is due primarily to exchange and polarization forces, and that ordinary electrostatic forces play a minor role.

1. INTRODUCTION

THE theory of the work functions of monovalent metals has been discussed in a recent paper[1] by E. Wigner and the author. This work was incomplete in two respects. In the first place, the free-electron values were used for the Fermi, Coulomb, exchange and correlation energies of the metal. This defect could be removed by making explicit calculations of these energies for the different metals. Such calculations have been carried out, at least in part, for Na,[2, 3] Li,[4, 5] and Cu.[6, 7] Secondly, the electrostatic double layer at the surface of the metal was left undetermined.

The main object of the present work is to show how the double layer is determined and to make a rough calculation of the moment of the double layer at the surface of an ideal metal. The charge distribution at the surface is calculated by the method of the self-consistent field based on the Fock equations. This calculation may be of some interest, not only in the present connection, but also because it yields some information about the potential barrier at the surface of the metal.

In the previous paper, the work function was obtained by first calculating the energy $E(n_i, n_e)$

* Society of Fellows. The major part of this work was completed while the author was a Fellow in Mathematics at Princeton University.

[1] E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935).
[2] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).
[3] J. C. Slater, Phys. Rev. **45**, 794 (1934).
[4] F. Seitz, Phys. Rev. **47**, 400 (1935).
[5] J. Millman, Phys. Rev. **47**, 286 (1935).
[6] H. M. Krutter, Phys. Rev. **48**, 664 (1935).
[7] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).

of a metal containing n_i ions and n_e electrons. This calculation required but a slight modification of the method used by Wigner and Seitz[8] for calculating the energy of an uncharged metal. The work function, φ, was then easily obtained, as

$$\varphi = -(\partial E(n_i, n_e)/\partial n_e)_{n_i=n_e}. \quad (1)$$

It was shown that the work function consists of two parts, the "binding energy" of the electron, and the energy required to move the electron through an electrostatic double layer at the surface of the metal. The first part may be calculated without reference to the surface, and this has been carried out in (I). In order to determine the moment of the double layer, it is necessary to make an explicit calculation of the charge density at the surface.

As our model for the present calculation, we suppose that the metal occupies the half-space on the negative side of the Y-Z plane. The density of positive electricity is constant for $x<0$ and is zero for $x>0$. This same model has been treated by Frenkel[9] from the standpoint of the Thomas-Fermi theory. We here determine the charge distribution at the surface from an approximate solution of the Fock equations. Our calculation also gives the work function of the model from a somewhat different viewpoint than that used in (I). The density of electrons assumed is approximately the same as the density of free electrons in Na, and a comparison is made of the work functions of our model and that of Na. An attempt is made to include the correlation (or polarization) forces which are neglected in the Slater-Fock approximation of one-electron wave functions.

2. Definitions

The work function may be defined (cf. I) as the difference in energy between a lattice with an equal number of ions and electrons, and the lattice with the same number of ions, but with one electron removed. It is assumed in both cases that the lowest electronic states are completely filled, so that the electron is removed from the highest energy state of the neutral metal. Since the work function may be different for different crystallographic planes, it is necessary to specify the position of the electron after its removal from the lattice. It is supposed that the electron is removed to a point in the neighborhood of a surface plane of the crystal, the distance from this plane being small compared with the dimensions of the plane, but large in comparison with atomic dimensions. The potential differences between the outer neighborhoods of differently oriented crystal surfaces will be equal to the differences of the work functions of these surfaces.

The moment of the electric double layer on the surface may be defined as the difference in potential between a point outside the surface and a point in the interior. This definition will serve for our free-electron model. As the potential in the interior of an actual metal is not constant in the interior, but is periodic, it is necessary to specify further the position of the interior point relative to the lattice. The position of this point is somewhat arbitrary, but once chosen, it fixes the otherwise arbitrary constant in the energy parameters of the wave equations for the different electrons which are valid in the interior of the metal. It will be sufficiently accurate to specify the position of the interior point with respect to the approximate model of Wigner and Seitz in which the actual metal is replaced by a set of close-packed spheres (the s spheres).[2] In each sphere, the potential will be a function only of the distance from the center of the sphere. As our interior point we shall take, as in (I), a point on the surface of the s sphere. This definition is most convenient, as it gives a zero moment if the electron-distribution in the s spheres of the surface ions is the same as that in the s spheres of the interior ions. The double layers are due to the fact that the actual distribution may extend outside the limits of the s spheres of the surface ions, and may have greater or smaller densities in the interior of these spheres.

The exact definition of the moment of the double layer is of importance in our connection when we compare the work function and double layer of our free-electron model with the corresponding quantities of the sodium crystal. We shall find that the work functions may be directly compared, but that, as a consequence of

[8] Cf. reference 2. A general review has been given by J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[9] J. Frenkel, Zeits. f. Physik **51**, 232 (1928). This paper also gives a discussion of the surface double layer.

the above definitions, the moment of the double layer of the 110-face of the sodium crystal is about 0.25 ev less than that of the free-electron model.

3. Magnitude of the Double Layers

Before proceeding with the calculation, it might be well to say a few words about the expected order of magnitude of the moment of the double layers. The most direct evidence was given in (I). It was found that the theoretical values of the work functions of the alkalies checked the experimental values very closely, even though the double layer was omitted entirely. This suggests that the double layers of these elements are probably small (less than half a volt).

Since the potential in the interior of a metal is constant (or, more accurately, periodic), the differences in the work functions of different surface planes of the same crystal are equal to the differences in the moments of the corresponding double layers. These differences, experimentally, are of the order of $\frac{1}{2}$ to 1 volt.[10] One might expect that the moments themselves are of this same order of magnitude.

On the other hand, experiments show that the value of the work function depends to a large extent on the condition of the surface.[11] Adsorbed gas or deposits of foreign material may alter the work function considerably. Ives and Olpin[12] and J. J. Brady[13] have shown that a monatomic layer of alkali atoms deposited on a metal may reduce its work function by as much as 50–75 percent. These data indicate that the work function of a surface is really determined by the top few layers of atoms, and not by the metal as a whole. The large changes in the work function due to different surface conditions, must, of course, be due to corresponding changes in the surface double layer. A knowledge of the charge distribution at the surface is thus really necessary for the determination of the work function. One may expect, however, that the distribution for pure metals will be such that the double layer is small.

4. The Free-Electron Model

The density of positive electricity has the constant value $e\rho_+$ in the half-space on the negative side of the YZ plane and is zero elsewhere. If the density of electrons is $\rho_-(x)$, the electrostatic potential, V, will be given by the solution of

$$d^2V/dx^2=-4\pi e\rho(x);\ \rho(x)=\begin{cases}\rho_+-\rho_-(x) & x<0,\\ -\rho_-(x) & x>0.\end{cases} \tag{2}$$

If the charge distribution is known, this equation may be solved for V. The boundary conditions are, if the metal is uncharged:

$$\begin{aligned} &V=0,\quad dV/dx=0 \quad \text{as} \quad x\to\infty, && \text{(a)}\\ &\qquad dV/dx=0 \quad \text{as} \quad x\to-\infty. && \text{(b)}\end{aligned} \tag{3}$$

Condition (3b) requires that[14]

$$\lim_{x\to-\infty}\int_x^\infty \rho(x)dx=0. \tag{4}$$

The constant value of the potential in the interior,[15] V^0, is, by definition, the moment of the surface double layer.

5. The Fock Equations

Our calculation of the charge density at the surface is based on the Slater-Fock[16] approximation of one-electron wave functions. An attempt is made, however, to correct for the correlation (or polarization) forces which are neglected in this approximation (cf. section 8). If there are n electrons which occupy $n/2$ doubly degenerate states, the Fock equations have the form:

$$(-(\hbar^2/2\mu)\Delta_i-eV(\mathbf{r}_i)-A_i)\psi_i(\mathbf{r}_i)=E_i\psi_i(\mathbf{r}_i), \tag{5}$$

where $V(\mathbf{r}_j)$ is the Coulomb potential of the combined positive and negative charges. If

$$\rho(\mathbf{r},\mathbf{r}_j)=\sum_i\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}_j) \tag{6}$$

[10] N. E. Farnsworth and B. A. Rose, Proc. Nat. Acad. Sci. **19**, 777 (1933); B. A. Rose, Phys. Rev. **44**, 585 (1933); N. Underwood, Phys. Rev. **47**, 502 (1935).

[11] See, for example, A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill, 1932), p. 72.

[12] H. E. Ives and A. R. Olpin, Phys. Rev. **34**, 117 (1929).

[13] J. J. Brady, Phys. Rev. **41**, 613 (1932).

[14] If the metal has a surface charge, the integral of Eq. (4) is no longer zero. In this case, condition (3a) is replaced by $dV/dx=4\pi\sigma$ as $x\to\infty$, where σ is the surface density of charge.

[15] The superscript zero will be used throughout to indicate values which apply in the interior.

[16] J. C. Slater, Phys. Rev. **34**, 1293 (1929); **35**, 210 (1930). V. Fock, Zeits. f. Physik **61**, 126 (1930). An excellent review has been given by L. Brillouin, *Les Champs "self-consistents" de Hartree et de Fock*, Actualités scientifiques (Herman, Paris, No. 159, 1934).

is the Dirac density matrix, the exchange operator A_i is defined by

$$A_i\psi_i(\mathbf{r}_i)=\frac{e^2}{2}\int\frac{\rho(\mathbf{r},\mathbf{r}_i)\psi_i(\mathbf{r}_i)d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_i|}. \qquad (7)$$

The sum in (6) is over all orbital wave functions, the spin factors being omitted. The factor $\frac{1}{2}$ appears in (7) because the exchange operator is effective only for electrons of parallel spin, while the wave functions of all electrons are summed in $\rho(\mathbf{r},\mathbf{r}_i)$. The density of electrons is $\rho_-(\mathbf{r})=\rho(\mathbf{r},\mathbf{r})$.

In the following, we shall use instead of the exchange operator, an exchange potential defined by:[17]

$$A_j(\mathbf{r}_j)=\frac{e^2}{2}\int\frac{\rho(\mathbf{r},\mathbf{r}_i)\psi_j(\mathbf{r})d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_i|\psi_i(\mathbf{r}_i)}. \qquad (8)$$

This exchange potential thus depends on the wave function, and will be different for different wave functions. The advantages of using the exchange potential rather than the exchange operator are two. First, the potential is easier to visualize physically. As Slater and Krutter[17] point out, the field acting on the electron is actually to be identified with the sum of the Coulomb and exchange potentials, rather than the Coulomb potential alone. There is a hole cut out of the charge distribution about each electron due to the fact that the probability of two electrons of parallel spin being close together is small. The total charge cut out by the hole is exactly e. The exchange potential is essentially the potential resulting from the hole.[18] The second reason is more practical. We want to find a self-consistent solution of these equations, and this must be obtained by numerical calculations. The exchange integrals are very difficult to evaluate directly. The procedure adopted was to approximate the actual set of wave functions by a set of analytic functions for which some of the required integrations could be performed. It was found that the exchange potentials were much less sensitive to the actual form of the wave functions than the exchange integrals.

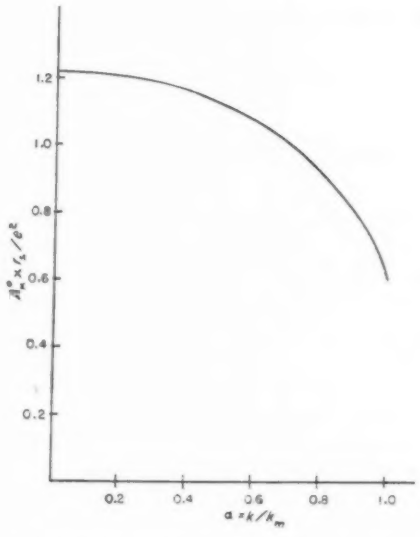

FIG. 1. Exchange potential in interior as a function of the velocity of the electron.

6. WAVE FUNCTIONS IN THE INTERIOR

We shall replace the actual infinity of wave functions for the free-electron model by a finite number by introducing periodic boundary conditions (period L) in the Y and Z directions, and a fixed boundary at $x=-L$. The wave functions in the interior[15] will be the plane waves

$$\psi_k{}^0(x,y,z)=2^{\frac{1}{2}}L^{-\frac{3}{2}}\sin(k_1x+\gamma)e^{i(k_2y+k_3z)}. \qquad (9)$$

The allowed values of k_2 and k_3 are $2\pi\nu_2/L$ and $2\pi\nu_3/L$ where ν_2 and ν_3 are integral. The allowed values of k_1 are $2\pi\nu_1/L$ where the values of ν_1 lie close to the half-integers $(\frac{1}{2}, 1, \frac{3}{2}, \cdots)$. We suppose that there are n electrons in the volume L^3 and that all states are doubly occupied from $\nu=0$ to $\nu=\nu_m$, where $\nu=(\nu_1{}^2+\nu_2{}^2+\nu_3{}^2)^{\frac{1}{2}}$ and $\nu_m=(3n/8\pi)^{\frac{1}{3}}$. The radius of the sphere (s sphere) whose volume is equal to the average volume occupied per electron is:

$$r_s=(3/4\pi n)^{\frac{1}{3}}L=1.92(2\pi\nu_m/L)=1.92k_m. \qquad (10)$$

[17] Cf. reference 8, and J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

[18] It should be emphasized that this interpretation cannot be made in all cases. The exchange potential defined in this manner may be complex or may have infinite values. In our case, the potential is real and finite. The probability of an electron in the jth state being in the volume element $d\mathbf{r}$, and a second electron being in the volume $d\mathbf{r}_1$ is the *real* part of:

$$\Sigma_i(\psi_i{}^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_j{}^*(\mathbf{r})\psi_j(\mathbf{r})-\psi_i{}^*(\mathbf{r}_1)\psi_i(\mathbf{r})\psi_j{}^*(\mathbf{r})\psi_j(\mathbf{r}_1))d\mathbf{r}d\mathbf{r}_1.$$

The second term represents the "hole."

We shall find it convenient to use r_s as a parameter which gives, indirectly, the density of the electrons.

The exchange potential in the interior is constant. The exchange operator acting on a wave function of the form (9) has the effect of multiplying the wave function by a constant. This constant, which has been evaluated by Dirac,[19] depends on the ratio $\alpha=k/k_m$ of the momentum of the given electron to the maximum momentum of the Fermi distribution. The value of the exchange potential in the interior is:

$$A_k{}^0=e^2k_mf(\alpha)/2\pi=0.306e^2f(\alpha)/r_s,$$

where

$$f(\alpha)=2+(1/\alpha)(1-\alpha^2)\log((1+\alpha)/|1-\alpha|). \quad (11)$$

A plot of $A_k{}^0$ as a function of α is given in Fig. 1.

The equation for $\psi_k{}^0$ is:

$$(-(\hbar^2/2\mu)\Delta-eV^0-A_k{}^0)\psi_k{}^0=E_k\psi_k{}^0, \quad (12)$$

so that $$E_k=(\hbar^2/2\mu)k^2-eV^0-A_k{}^0. \quad (13)$$

It may be noted here that, to the approximation of the Fock equations, the energy required to remove the kth electron from the metal is $-E_k$. The work function, φ, is the minimum value of $-E_k$, or

$$\varphi=-(\hbar^2/2\mu)k_m{}^2+eV^0+A_{k_m}{}^0. \quad (14)$$

This agrees, except for the correlation energy which we have so far neglected, with the results of (I).

7. Method of Calculation

The exchange potential decreases in magnitude as one approaches the surface, and goes to zero as $x\to\infty$. It is independent of y and z. The Fock equation (cf. Eq. (5)) thus has the form:

$$(-(\hbar^2/2\mu)\Delta-eV(x)-A_k(x))\psi_k(r)=E_k\psi_k(r) \quad (15)$$

with $V(x)$ given by (2) and (3) and E_k by (13).

Since the potential is independent of y and z, the wave functions must be of the form:

$$\psi_k(x, y, z)=\varphi(k, x)e^{i(k_2y+k_3z)}. \quad (16)$$

The equation for $\varphi(k, x)$ is

$$(-(\hbar^2/2\mu)(d^2/dx^2)-eV(x)-A_k(x))\varphi(k, x)$$
$$=(E_k-(\hbar^2/2\mu)(k_2{}^2+k_3{}^2))\varphi(k, x) \quad (17)$$

and the asymptotic form of $\varphi(k, x)$ in the interior is:

$$\varphi^0(k, x)=2^{\frac{1}{2}}L^{-1}\sin(k_1x+\gamma). \quad (18)$$

The phase, γ, may depend on k_2 and k_3 as well as k_1.

In order to obtain an accurate solution of Fock's equations, one takes a set of starting wave functions, and then computes the Coulomb and exchange potentials from these. The next approximation to the correct wave functions is obtained by solving Fock's equations using these potentials. This procedure is repeated until a self-consistent set of wave functions is obtained, i.e., a set such that the Coulomb and exchange potentials computed from these wave functions are the same as the potentials used in deriving the wave functions. Because of the numerical difficulties involved in evaluating the exchange integrals, it was not found feasible to carry out this process in full.

Instead, the exchange potentials were chosen at the beginning and held fixed throughout. A self-consistent solution was then obtained for the electrostatic part of the problem. In the final stage, the Coulomb potential calculated from the final wave functions was equal to the potential used in determining these wave functions. The exchange potentials were determined from an approximate set of wave functions which will be described in the next section. As the charge distribution corresponding to these approximate wave functions is fairly close to the calculated charge distribution, one may expect that the exchange potentials as determined from the two sets of wave functions are also very nearly the same. The Fermi hole is very large near the surface, and so should not be sensitive to the exact form of the wave functions at the surface.

8. Calculation of Exchange Potentials

As one approaches the surface of the metal, the Fermi hole will increase in volume in such a way that a total charge e is always cut out by the hole. The shape of the hole will depend not only on the speed of the electron, but also on its direction. The dependence on direction is rather small, and is unimportant for our purpose. The exchange potential of an electron whose motion is perpendicular to the surface will drop a little more

[19] P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930).

slowly than the potential of an electron of the same energy whose motion is parallel to the surface, but the drop will start sooner, so that the potentials of the two electrons will be about equal half-way down the slope. We shall, in our work, neglect this dependence on direction.

It is very difficult to evaluate the exchange potentials for wave functions other than the plane waves discussed above. It is possible, however, to get some idea of the behavior of the exchange potentials by calculating $A_k(x)$ for the wave functions of a somewhat simplified model. We shall suppose that the electrons move in a constant negative potential, W, for $x<a$ and that the potential is zero for $x>a$. The position of the barrier, a, and the height of the barrier, W, are adjusted in such a way that the wave functions and charge distribution of this simplified model correspond most closely with the wave functions of the free-electron model. The integrals are so complicated, even for this simple model, that it is difficult to evaluate them except at the potential wall, $x=a$.

Instead of using x as a coordinate, we shall use $\xi=x-a$, so that the barrier is at $\xi=0$. The wave functions are then of the form (16) with

$$\varphi(k,\xi)=\begin{cases}2^{\frac{1}{2}}L^{-\frac{1}{2}}\cdot(1/p)(-(p^2-k^2)^{\frac{1}{2}}\sin k\xi \\ \qquad\qquad +k\cos k\xi) & \xi<0, \\ 2^{\frac{1}{2}}L^{-\frac{1}{2}}(k/p)e^{-(p^2-k^2)^{\frac{1}{2}}\xi} & \xi>0,\end{cases} \quad (19)$$

where
$$p^2=-2\mu W/\hbar^2. \quad (20)$$

The integrals we must evaluate are those of Eq. (7).

$$A_k(\xi)\psi_k(\mathbf{r})=\frac{e^2}{2}\sum_l\int\frac{\psi_l^*(\mathbf{r}_1)\psi_l(\mathbf{r})\psi_k(\mathbf{r}_1)d\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}. \quad (21)$$

The summation over l is over all occupied states, and may be replaced by an equivalent integration over a sphere S of radius $k_m=(2\pi/L)(3n/8\pi)^{\frac{1}{3}}$. ($n$ is the number of electrons in the volume L^3.) It is shown in the appendix that if we replace ψ_k by (16) and then integrate over y_1, and z_1, that we have:

$$A_k(\xi)\varphi(k,\xi)=\frac{e^2L^3}{4\pi^2}\int d\xi_1\int_S\varphi(l,\xi_1)\varphi(l,\xi) \times\varphi(k,\xi_1)(e^{-\lambda|\xi-\xi_1|}/\lambda)dl_1dl_2dl_3, \quad (22)$$

where $\lambda^2=(l_2-k_2)^2+(l_3-k_3)^2$.

The integration over l_2 and l_3 is difficult to carry out in general unless $k_2=k_3=0$, or, in other words, unless the electron is moving in a direction perpendicular to the surface. Since the exchange potential of an electron depends mainly on its velocity, one may obtain a good approximation for arbitrary k_2, k_3 by first carrying out the integration with k_2 and k_3 set equal to zero, and then replacing k_1 by $(k_1^2+k_2^2+k_3^2)^{\frac{1}{2}}$ in the final result. If $k_2=k_3=0$, the integral (22) reduces to:

$$A_k(\xi)\varphi(k,\xi)=\frac{e^2L^3}{2\pi}\int_{-\infty}^{+\infty}d\xi_1\int_{-k_m}^{k_m}dl_1\int_0^{(k_m^2-l_1^2)^{\frac{1}{2}}} \times d\lambda e^{-\lambda|\xi-\xi_1|}\varphi(l_1,\xi_1)\varphi(l_1,\xi)\varphi(k_1,\xi). \quad (23)$$

The integration over λ may be also carried out, but before doing this it is best to substitute the expressions (21) for $\varphi(l_1,\xi)$ and then integrate over ξ_1. The integration over λ may then be carried out at $\xi=0$. If one then divides by the value of $\varphi(k,\xi)$ at $\xi=0$, one obtains the following integral for $A_k(0)$.

$$A_k(0)=\frac{e^2}{\pi p^2}\int_{k_m}^{k_m}\Big\{\frac{k}{l}-[\tfrac{1}{2}(BC+kl) \times\log((k_m^2+l^2-2kl)/(k-l)^2) +(lB-kC)\tan^{-1}(D/(k-l))] +k^2\log((B+C+D)/(B+C))\Big\}dl \quad (24)$$

where $B=(p^2-k^2)^{\frac{1}{2}}$, $C=(p^2-l^2)^{\frac{1}{2}}$, $D=(k_m^2-k^2)^{\frac{1}{2}}$. The last integration may be carried out if $p=\infty$, i.e., if the barrier at $\xi=0$ is infinite. In this case

$$A_k(0)=(e^2k_m/\pi)[\tfrac{3}{4}-1/4\alpha^2+(1/8\alpha^3) \times(1+2\alpha^2-3\alpha^4)\log((1+\alpha)/|1-\alpha|)], \quad (25)$$

where $\alpha=k_1/k_m$. It can be shown that this last equation is rigorously correct for electrons of *arbitrary* direction if $\alpha=(k_1^2+k_2^2+k_3^2)^{\frac{1}{2}}/k_m$.

Fig. 2 gives the variation of the exchange potential with α for $p=\infty$ and for $p=1.15k_m$. The latter were obtained by numerical integration. The wave functions for $p=1.15k_m$ correspond most closely with the computed wave functions of the free-electron model.

These data enable one to get a reasonably good picture of the way in which the exchange poten-

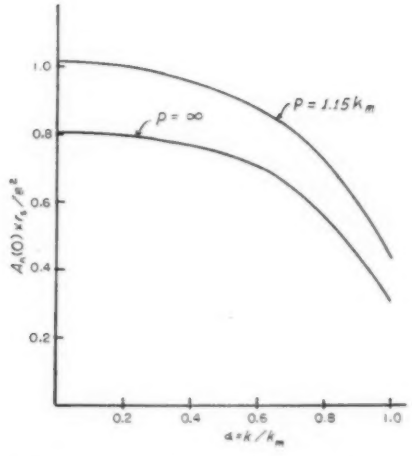

FIG. 2. Exchange potentials at the barrier for $p=1.15k_m$ and $p=\infty$.

tials vary near the surface of the metal. The exchange potentials for wave functions of the type we are considering depend mainly on the charge distribution, and not on the exact form of the wave functions at the surface. The Fermi hole is so large that any local irregularities are ironed out when one integrates over the hole to obtain the potential.

The position of the barrier is at $\xi=0$ or at $x=a$. The value of a is fixed for any value of p by the requirement that the metal be neutral, i.e., the requirement of Eq. (4). It may be shown by straightforward calculation that this gives:

$$a=(3/2k_m^3)[\pi k_m^2/4 - (k_m^2-p^2/2)\sin^{-1}(k_m/p)-\tfrac{1}{2}(p^2-k_m^2)]. \quad (26)$$

If $p=\infty$, $a=3\pi/8k_m=0.61r_s$. Similarly if $p=1.15k_m$, $a=0.11r_s$.

If the positions of the barriers are fixed in this manner, the exchange potentials are rather insensitive to the value of p. The values of the exchange potentials have been computed for $p=\infty$ at a point a distance $0.5r_s$ behind the barrier, or at $x=0.11r_s$. These values, obtained by numerical integration, agreed to within one percent with those computed at the same point for $p=1.15k_m$.

In the actual calculation, the positions of the barriers were taken at points slightly different from those given above. The wave functions corresponded more closely with those of the free-electron model with the barriers placed at $a=0.58r_s$ and at $a=0.08r_s$ for $p=\infty$ and for $p=1.15k_m$, respectively, instead of at points a distance $0.03r_s$ further out. The difference, however, is very slight, and hardly enough to affect the results appreciably.

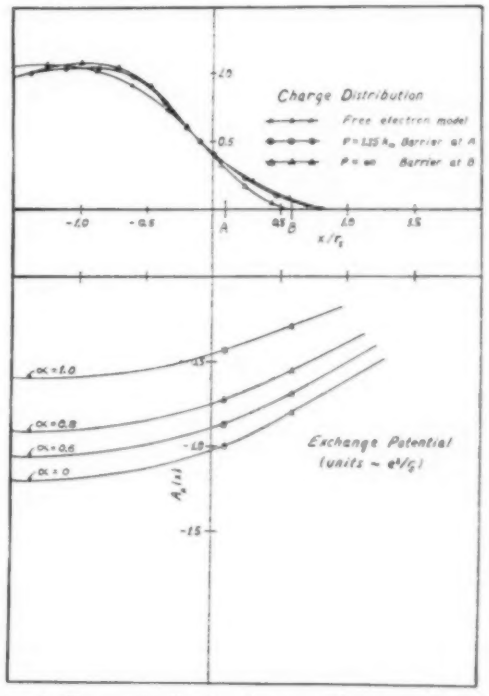

FIG. 3. Charge distributions for approximate wave functions and exchange potentials adopted.

Fig. 3 shows the charge distributions for $p=\infty$ and $p=1.15k_m$ as well as the charge distribution for the free-electron model which will be discussed at more length later on. The charge distributions match fairly well, so that it may be expected that the exchange potentials will also agree.

The exchange potentials which have been adopted are also shown in Fig. 3. These were obtained by drawing smooth curves through the known points at $x=0.08r_s$ and at $0.58r_s$ in such a way that they are asymptotic to the known values of the exchange potentials in the interior, and to zero for large positive values of x. The circles represent the values of the exchange potentials for $p=1.15k_m$ as taken from the curve of Fig. 2. The triangles represent the corresponding values for $p=\infty$. One would, of course, expect

that the circles are closer to the actual exchange potentials than the triangles, but the latter are probably not far off. This method for obtaining the exchange potentials is, of course, very rough, but it was not thought advisable to attempt a more accurate calculation at the present time.

Before discussing the solution obtained, we shall, in the next section, discuss the modification introduced by the correlation or polarization forces which we have so far neglected.

9. The Correlation Energy

Because of electrostatic repulsion, electrons tend to keep as far away from each other as possible. In the Slater-Fock approximation, electrons of parallel spin keep apart because of the exchange effect. There is, however, no allowance for the interaction of electrons of one spin with those of opposite spin except that resulting from the integrated charge distribution. The correlation energy of a metal is the energy gain in the binding energy of a metal which results from the use of a more general wave function than the Slater determinant of one-electron wave functions. Wigner[20] computed this energy for free electrons by using a wave function which allowed for a statistical correlation of the positions of the electrons of one spin with those of opposite spin. The direct contribution of the correlation hole to the work function, computed in (I), is

$$e^2 f(r_s) - e^2 r_s f'(r_s)/3, \tag{27}$$

where $r_s f(r_s)$ is the correlation function of Wigner.[20]

The correlation hole will also influence the charge distribution at the surface, and therefore the double layer. This latter effect seems to be very difficult to take rigorously into account, because to do so it would be necessary to abandon the one-electron wave functions we have used so far. One would expect, however, that the influence on the charge distribution could be approximately taken into account by an appropriate modification of the potential curves for the one-electron wave functions. This modification would be such as to lower the potential in the interior of the metal. At large distances from the surface, the combined potential of the exchange and correlation forces should go over into the image potential, $-e^2/4x$.

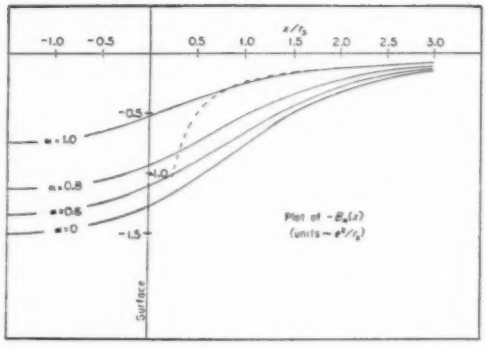

FIG. 4. Combined exchange and correlation potentials ($r_s=4$ Bohr units).

The amount the potential is lowered in the interior will depend on the velocity of the electron, and will be smaller for electrons of high velocity than for those of lower velocity. In the following work we shall make the crude approximation that the correlation potential varies in the same way with velocity and position as the exchange potential in the interior and at small distances from the surface of the metal, and that at large distances from the surface the combined correlation and exchange potential approaches the image potential asymptotically.[21] In other words, we shall replace $A_k(x)$ in Eq. (17) by a potential $B_k(x)$ where

$$B_k(x) = (1+c)A_k(x) \tag{28}$$

except for large x, and we assume that when x is large, $B_k(x) \sim e^2/4x$. We shall take for c the ratio of the correlation to the exchange energy of the free-electrons. If $r_s=4$ Bohr units, $c=0.24$.

Fig. 4 gives the potentials $B_k(x)$ for several values of x which were obtained from the exchange potentials, $A_k(x)$, of Fig. 3 by the method described above. These curves apply for $r_s=4$ Bohr units.[22]

[20] E. Wigner, Phys. Rev. **46**, 1002 (1934). The correlation function is represented by the lower curve of Fig. 7.

[21] J. C. Slater has suggested a treatment along these lines. Cf. reference 8.

[22] The curves for the smaller values of α should probably approach the image potential more rapidly than I have indicated. This modification would make little difference in the present connection, but should be borne in mind if these curves are put to some other use. The author is indebted to Professor Slater for this remark.

10. The Self-Consistent Solution

Two solutions of Eqs. (17) have been obtained, one using the exchange potentials of Fig. 3, and the second using $B_k(x)$ of Fig. 4. The first solution was very rough, and served only to indicate the order of magnitude of the moment of the double layer. The Coulomb potential of the second was self-consistent to within $\pm 0.01 e^2/r_a$. The density of electrons in both cases was taken to be approximately equal to the density of free-electrons in Na, assuming one free-electron per atom, the actual value corresponding to $r_a=4$.

The solutions were obtained in the following manner. One first assumes a charge distribution for the electrons, and then calculates the Coulomb potential, $V(x)$, by integration of Eq. (2). Eq. (17) is then integrated numerically from large positive values of x into the interior, where $\varphi(k, x)$ must join smoothly with the solution in the interior, sin $(k_1 x+\gamma)$. This requirement determines the amplitude of the wave function, and also the phase, γ, of the plane wave in the interior. The integration is carried out for a sufficient number of values of k_1, k_2, k_3, so that one may integrate over the occupied states and obtain the charge distribution. If this calculated distribution checks the assumed distribution, the problem is solved. If not, a new distribution is assumed, and the wave functions and charge distribution are redetermined. This process is repeated until a self-consistent solution is obtained. The exchange potentials $A_k(x)$ (or $B_k(x)$) are held fixed throughout.

In order to determine an accurate self-consistent solution of Fock's equations, the exchange potentials should also be redetermined from the calculated wave functions, but this involves a difficult numerical integration and has not been carried out.

In the pure Fock case, the exchange potentials $A_k(x)$, are used, and the work function, φ, is

$$\varphi = -(\hbar^2/2\mu)k_m^2 + eV^0 + A_{km}^0. \qquad (29)$$

Rough calculations that have been carried out indicate that the moment of the double layer, eV^0, is about one volt for $r_a=4$. The maximum value of the Fermi energy, $\hbar^2 k_m^2/2\mu$, is 3.15 ev. The exchange energy of the electron of maximum velocity is $0.61\ e^2/r_a=4.1$ ev. Thus if we neglect the correlation energy entirely, the work function will be about two volts. If we include the direct contribution of the correlation energy (cf. section 8) the work function is about three volts.

It is not altogether reasonable to include the direct contribution of the correlation energy if we omit it in the calculation of the surface double layer (V^0) because the work function is rather insensitive to the exchange potential employed. Our neglect of the correlation energy has been partly compensated by a large V^0. If we had omitted the exchange energy, we would still obtain a positive (though probably small) value for the work function with a very large V^0 ($\sim$4 volts).

The solution obtained when the potentials $B_k(x)$ of Fig. 4 were used is illustrated in Fig. 5. The potential curves shown include the Coulomb potential, $V(x)$. The moment of the double layer, V^0, is $0.06 e^2/r_a$, or about 0.4 volt. The value of

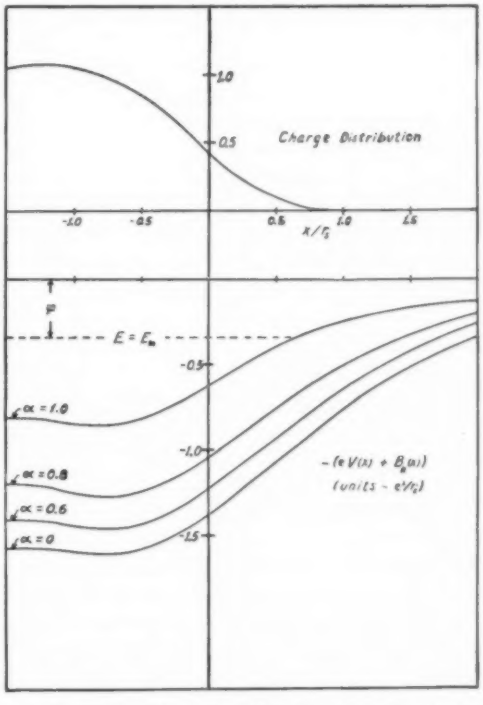

FIG. 5. Self-consistent charge distribution and potentials for the free-electron model ($r_a=4$ Bohr units). The potential curves shown include the exchange and correlation potentials of Fig. 4 and the Coulomb potential of the charge distribution.

the work function is then 2.35 volts, if we include the direct contribution of the correlation energy (1.0 ev).

11. Comparison with Sodium

It has been shown by Wigner and Seitz[2] and by Slater[3] that the wave functions of the conducting electrons of the sodium crystal are, except in the immediate vicinity of the ions, very nearly the same as those of perfectly free electrons. The density of electrons is practically uniform throughout the crystal. The Fermi energy is within one or two percent of the classical free-electron value, $3\hbar^2k_m^2/10\mu$. The exchange potentials are very nearly constant in space, and are close to the free-electron values in magnitude. One would thus expect that the free-electron model which has been discussed in the preceding sections would bear a close relationship with the sodium crystal.

Since the exchange potentials are constant in the interior of the lattice, the Fock equations are identical with the Hartree equations. The exchange terms affect the energies of the electrons, but not the wave functions. If we omit the exchange terms, the potential field in which the electrons move is the combined potential of the ions and the Coulomb potential of the electrons. Wigner and Seitz replace the actual (body-centered) lattice by a set of close packed spheres. They found that if the zero of potential is taken on the surface of an s sphere, the energy of the lowest state is $E_0=-0.23$ ev. The actual potential on the surface of an s sphere, relative to a point outside one of the faces of the crystal, will differ from zero by the moment of the double layer of this face.

The work function, φ, is (cf. (I)):

$$\varphi_{Na}=-E_0+eD+A_{k_m}{}^0+C-\hbar^2k_m^2/2\mu, \quad (30)$$

where we have written C for the contribution from the correlation energy, and eD for the moment of the double layer. The only difference between (30) and the corresponding formula for the free-electron model is that $-E_0+eD$ replaces eV^0 of the latter.

One might at first be tempted to identify eV^0 with eD. Some care must be taken, however, as the definitions of the moments in the two cases are slightly different. Thus eD will be zero if the distribution of electrons in the surface s spheres is the same as that in the inner s spheres, while eV^0 will be zero if the distribution is constant for $x<0$ and zero for $x>0$. For the same distribution of electrons, eD will be somewhat smaller than eV^0. The difference can be computed for any face of the crystal, and it amounts to approximately 0.25 ev for the 110-face. Values for other faces are slightly larger.

Thus $-E_0+eD$ for the 110-face should be about the same as eV^0, while the corresponding values for other faces should be a little less. This, of course, rests on the assumption that the electronic charge distribution at the surface of the sodium crystal is approximately equal to that of the free-electron model. Calculations that have been attempted for the 110-face indicate that this assumption is justified.

Table I summarizes the results that have been obtained for the free-electron model, together with the rather uncertain experimental values of the work function of sodium. The agreement is very satisfactory, considering the approximate nature of the theory. The moment listed for sodium was obtained by reducing the value for the free-electron model (0.4 volt) by 0.25 volt.

Table I. *Comparison of theoretical values of the work function of the free-electron model with experimental values for sodium.*

	Free-Electron Model, Correlation Forces Omitted	Free-Electron Model, Correlation Forces Included	Sodium (exp.)
Moment of double layer	1.0	0.4	(0.15)
Work function	2.0	2.35	2.46*
			2.25†

* A. R. Olpin, see reference 11, p. 75.
† Z. Berkes, Math. Phys. Lapok **41**, 131 (1934).

12. Conclusions

The following are the main results obtained from the present investigation of the free-electron model:

(1) The barrier at the surface is due largely to exchange and polarization forces, rather than to ordinary electrostatic forces.

(2) There is no single potential barrier which is satisfactory for electrons of all velocities. Each electron has, so to speak, its own barrier.

(3) The moment of the double layer at the surface is relatively small, in agreement with the conclusions reached in reference I. This, of course, means that the ordinary electrostatic potential in the interior is small.

(4) Approximate agreement is obtained between the work function of the free-electron model and the experimental values of the work function of sodium.

The writer wishes to express his gratitude to Professor E. Wigner, under whose direction this work was carried out, and to Professor J. H. Van Vleck, Professor J. C. Slater, and Dr. F. Seitz for interesting discussions.

Appendix

Evaluation of the integral:

$$I=\int\int\frac{e^{i[(k_2-l_2)(y-y_1)+(k_3-l_3)(z-z_1)}}{((\xi-\xi_1)^2+(y-y_1)^2+(z-z_1)^2)^{\frac{1}{2}}}dy_1dz_1.$$

This integral is not absolutely convergent, and in evaluating it one must be careful to introduce polar coordinates, θ, ρ in place of y_1 and z_1 and then integrate first over θ. If one chooses the origin of θ properly, the integral takes the form:

$$I=\int_0^\infty\rho d\rho\int_{-\pi}^{\pi}\frac{e^{i\lambda\rho\cos\theta}}{((\xi-\xi_1)^2+\rho^2)^{\frac{1}{2}}}d\theta$$

with $\lambda^2=(k_2-l_2)^2+(k_3-l_3)^2$. The integration over θ gives Bessel's function $J_0(\lambda\rho)$. We thus have:

$$I=2\pi\int_0^\infty\frac{\rho J_0(\lambda\rho)d\rho}{((\xi-\xi_1)^2+\rho^2)^{\frac{1}{2}}}=(2\pi/\lambda)e^{-\lambda|\xi-\xi_1|}.$$

Eq. (22) follows immediately.

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The Variation of Young's Modulus with Magnetization and Temperature in Nickel

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The relation between Young's modulus, magnetization, and temperature in annealed polycrystalline nickel, 99.7 percent pure, is determined for values of J between zero and saturation, and for values of T between 23.5°C and 400°C. The percent increase in Young's modulus is proportional to J^2 between zero and about 0.4 saturation, at all temperatures below 311°C. The total increase in the modulus from the demagnetized to the saturated state is 6.7 percent at 23°, reaches a maximum of 18.7 percent at 185°, and decreases to zero at the Curie point. The results indicate that the theory of this phenomenon offered by Akulov is probably essentially correct but requires modification. The method employed for the measurement of Young's modulus yields at the same time a measure of the coefficient of internal friction of the material. The internal friction decreases with increasing magnetization at all temperatures below the Curie point. In the demagnetized material it reaches a maximum value at the same temperature as does the change in elastic modulus. Its value at magnetic saturation is the same order of magnitude as that of a nonferromagnetic substance.

THE domain theory of ferromagnetism, first suggested by Webster in connection with magnetostriction and since developed by Heisenberg, Akulov and others, is noteworthy for its success in correlating different ferromagnetic phenomena in both single and polycrystalline materials. For example, Akulov[1] has shown that the change of Young's modulus with magnetization in a polycrystalline substance can be described solely in terms of the initial susceptibility and one magnetostrictive constant of a single crystal. The present paper is a report of an experimental investigation of the relation between Young's modulus and magnetization in annealed polycrystalline nickel at various temperatures below the Curie point. The results are compared with the formulae of Akulov's theory.

[1] Akulov, Zeits. f. Physik **85**, 661 (1933).

Experimental Method

The research consists in ascertaining the value of the Young's modulus, E, corresponding to an intensity of magnetization, J, and a temperature, T, for values of J lying between zero and technical saturation, and values of T ranging from 20°C to 400°C. Accordingly the experimental method must permit the simultaneous measurement of E, J, and T. To this end a preliminary determination is made of the relation between J, T and the normal magnetic induction, B, so that in the subsequent procedure a knowledge of B and T suffices to fix the value of J.

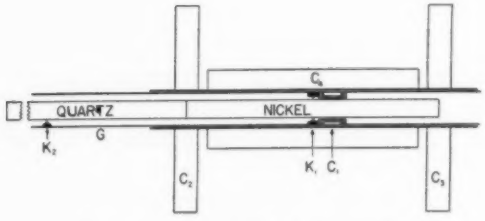

FIG. 1. Cross section of the assembly.

A specimen is prepared in the form of a right circular cylinder 0.464 cm in diameter and 7.2 cm long terminated by the end sections of a coaxial ellipsoid of revolution. The form approximates that of an ellipsoid of revolution whose major axis is 17.8 cm and minor axis is 0.464 cm. The specimen is mounted axially in a tubular electric furnace surrounded by a solenoid, and the variation of the normal magnetic induction with temperature and applied magnetizing field, H_0, is measured with a fluxmeter galvanometer. Corresponding values of J are then calculated with the formula $J=(B-H_0)/(4\pi-N)$, where N is the demagnetization factor of the ellipsoid, assumed the same as that of the specimen. The latter assumption is justified by the observed uniformity of B over the length of the cylinder, and by the fact that, since $N=0.028$, an error in the first significant figure would alter the calculated value of J by less than 0.1 percent. After these measurements are completed the cylindrical part of the specimen is sawed out and its ends ground flat.

The method employed for the measurement of Young's modulus is a modification of that previously described in this journal by Zacharias.[2] The specimen cylinder of nickel forms one part of a composite piezoelectric oscillator constructed by cementing to one end a cylinder of crystalline quartz of square cross section equal in area to that of the specimen. The quartz cylinder is so cut from the crystal that the optic axis lies perpendicular to one pair of opposite faces and an electric axis to the other, and the latter pair is coated with gold leaf. An harmonically varying potential difference of constant amplitude is established between the gold leaf electrodes, and means are provided for measuring the amplitude of the resulting current. In consequence of the harmonically varying piezoelectric stress in the quartz, produced by the electric field between the electrodes, the entire oscillator assumes a state of forced longitudinal vibration, the frequency of which is the same as that of the applied potential difference.

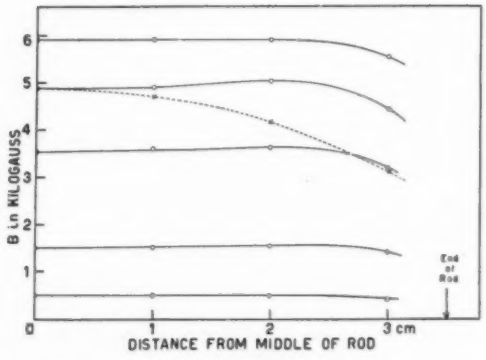

Fig. 2. Distribution of magnetic flux in the specimen. The dotted curve shows the distribution when the specimen is placed in a long solenoid.

The amplitude of the current which flows to the quartz varies critically with frequency in the neighborhood of certain "resonance frequencies" at which the amplitude of the vibration passes through a maximum. If f_0 denote one of these frequencies, then at a frequency f' slightly less than f_0 the current passes through a maximum, and at a frequency f'' slightly greater than f_0 it passes through a minimum. It is shown in Zacharias's paper that if I' and I'' denote, respectively, the maximum and minimum values of the current amplitude, then f_0 is given by the formula[3]

$$f_0=f'+I''(f''-f')/(I'+I''). \quad (1)$$

Furthermore, the fundamental frequency, f_1, of free longitudinal vibration of the nickel cylinder *alone* is related to f_0 by the formula

$$m_1 f_1 \tan(\pi f_0/f_1)+m_2 f_2 \tan(\pi f_0/f_2)=0, \quad (2)$$

where m_1 and m_2 are the masses, respectively, of the nickel and quartz cylinders, and f_2 is the fundamental frequency of free longitudinal vibration of the quartz cylinder alone. The value of f_2

[2] J. Zacharias, Phys. Rev. **44**, 116 (1933). Other papers on the use of composite piezoelectric oscillators for the measurement of elastic constants are: L. Balamuth, Phys. Rev. **45**, 715 (1934); and F. C. Rose, Phys. Rev. **49**, 50 (1936).

[3] Misprints which occur in Eqs. (11) and (12) of Zacharias' paper are here corrected.

is obtained by observing the current which flows to the quartz without the specimen attached. Lastly, the quantity f_1 is related to the Young's modulus of the material by the formula

$$E=4l^2f_1^2\rho, \quad (3)$$

where l is the length of the specimen cylinder and ρ is its density.

This method for measuring Young's modulus yields at the same time the value of the logarithmic decrement, δ, of free longitudinal vibration of the specimen cylinder. Thus

$$\delta=2\pi(1+m_2/m_1)\{(f''-f_0)(f_0-f')\}^{\frac{1}{2}}/f_0. \quad (4)$$

The coefficient of internal friction of the material is equal to δ/E.

Errors introduced by the adhesive and by inequality of areas at the interface are minimized by adjusting the lengths of the cylinders so that $f_1=f_2$ within 10 percent. These frequencies lie in the neighborhood of 36 kilocycles.

Fig. 1 is a cross-sectional diagram of the assembly upon which the measurements are made. The composite oscillator is mounted in a thin glass tube, G, upon an annular duralumin knife-edge, K_1, and a straight knife-edge, K_2, located at displacement nodes of vibration. The temperature of the specimen is measured with a Chromel-P *vs.* Alumel thermocouple in contact with the knife-edge K_1. The magnetic induction is measured with a fluxmeter galvanometer connected to the coil C_1, constructed by winding 90 turns of No. 40 chromoxide covered copper wire on a thin cylinder of baked lavite. The magnetizing coils C_2, C_3, and C_4 are designed to secure as nearly as possible a uniform magnetization over the length of the specimen cylinder. C_2 and C_3 are each 92 turns of copper ribbon 0.023 cm thick and 0.635 cm wide, insulated with thin strips of mica. C_4 is 340 turns of No. 20 chromoxide covered copper wire wound in 6 layers 5 cm long on a Pyrex tube 1 cm in diameter. The layers of this coil are also separated by mica sheet. The magnitudes and directions of the end and middle coil currents are so adjusted that B is uniform to 5 percent over eight-tenths the length of the specimen, at all temperatures and for all values of B. Typical distribution curves for B are shown in Fig. 2.

The assembly shown in Fig. 1 is placed in a rectangular duralumin oven, the interior dimensions of which are 7 in.×7 in.×12 in. The oven is heated electrically over its entire outer surface with grids formed by laying No. 22 constantan wire along parallel grooves cut in sheet transite. The outer thermal lagging is corrugated asbestos paper built up to a thickness of 1.75 in.

The voltage applied to the quartz crystal is supplied by a vacuum tube oscillator whose frequency can be varied in the neighborhood of f_0 by means of a variable condenser. As noted above, the determination of E requires the measurement of the maximum and minimum piezoelectric oscillator current amplitudes, and the frequencies at which these values occur. In previous applications of the method, the recording device for measuring the currents has been a d'Arsonval galvanometer, used in connection with a vacuum thermocouple or other rectifier. In the present instance, however, the heat produced by the current in the magnetizing coils changes the temperature of the specimen too rapidly to permit the use of this instrument. The entire set of observations must be made within six seconds after the magnetizing field is applied. This is accomplished in the following manner:

The difference of potential across a nonreactive resistance in series with the crystal is amplified and rectified with a vacuum tube rectifier. The rectified voltage is, in turn, ampli-

FIG. 3. Polar oscillogram of the piezoelectric oscillator current amplitude.

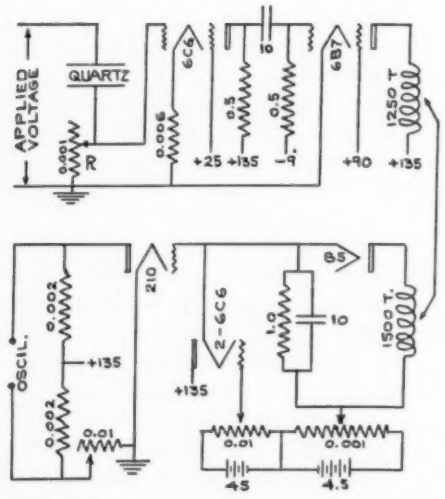

FIG. 4. The amplifying circuit. Resistances are in megohms and capacities in millimicrofarads.

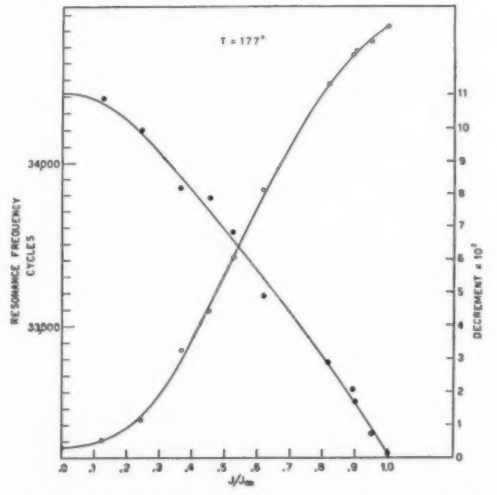

FIG. 5. Curves showing the resonance frequency (circles) and decrement (dots) of the piezoelectric oscillator as functions of magnetization at 177°C.

fied and energizes a General Electric Company Type PM-11 supersensitive oscillograph element. The light beam from the oscillograph passes through a cylindrical lens and falls upon a sheet of bromide paper attached to a vertical circular disk. This disk is mounted centrally on one end of the horizontal shaft of the variable condenser which controls the exciting frequency. An electric motor rotates the condenser at a rate which carries the frequency through f', f_0, and f'' in 4 seconds. During this time the light beam traces on the sensitized paper a polar diagram of the piezoelectric current amplitude, in which the angular coordinate is proportional to frequency and the radial coordinate to current. The condenser is frequency calibrated by comparison with the output of a piezoelectric clock,[4] and frequency calibration marks are placed on the record by illuminating it locally for an instant through short diametrically opposed radial slits.[5] A typical oscillogram is reproduced in Fig. 3.

Fig. 4 is a diagram of the amplifying circuits employed. The rectified voltage corresponding to an oscillator current amplitude between I' and I'' is balanced out with the 10,000-ohm potentiometer, so that only the fluctuation associated with I' and I'' is recorded by the oscillograph. The deflection of the oscillograph mirror varies linearly with the amplitude of the potential difference across the resistance, R, in series with the oscillator, and so with that of the current. Furthermore, the current is independent of the magnitude of R, since the latter is small in comparison with the impedance of the oscillator. Accordingly each oscillogram is current calibrated by noting the values of R required to duplicate the deflections corresponding, respectively, to I' and I'', the current being held constant at the intermediate value. The actual working formula for the calculation of f_0 is thus, from Eq. (1),

$$f_0 = f' + R''(f''-f')/(R'+R''), \qquad (5)$$

where R' and R'' correspond to the deflections associated, respectively, with I' and I''.

The experimental procedure is as follows: The temperature of the oven is stabilized, the specimen is placed in the desired state of magnetization on the normal induction curve by repeated reversals of the magnetizing current, and the resonance current record is taken immediately. The flux density, B, is then measured, the oven is allowed to resume its former equilibrium

[4] Quimby, Phys. Rev. 39, 345 (1932).

[5] It should, perhaps, be noted that this polar oscillograph is made fully automatic in operation by employing the various features of an RCA model 86 remote control radio unit. The different station selector contacts serve to start and stop the motor, flash the light source, open the source slit, etc.

temperature, and the process is repeated for various values of J. The oscillograph records are reduced with the aid of Eqs. (5) and (4), and curves are plotted, of which those shown in Fig. 5 are typical, showing f_0 and δ as functions of J/J_∞, where J_∞ denotes the saturation magnetization at the temperature of observation. Lastly, isothermals of this sort are obtained at various temperatures.

Results

The specimen material upon which the observations here reported were made is Mond nickel containing 0.295 percent impurity distributed as follows:[6] Co, 0.00; Si, 0.01; Cu, 0.02; Fe, 0.11; Mn, 0.00; C, 0.049; Mg, 0.11; S, 0.005. The specimen was annealed at 1100°C for 4 hours in hydrogen at atmospheric pressure and allowed to cool to room temperature in 18 hours. Microscopic examination reveals it to be an array of crystals whose average linear dimensions are 0.4 mm. The coercive force is 0.3 oersted, and the remanent intensity of magnetization is in the neighborhood of 9 gauss. The Curie point is 353°C, as determined to within one degree by the magnetic measurements and by the change of Young's modulus with magnetization and temperature. The variation of J_∞ with temperature is given by the first two columns of Table I.

The variation of Young's modulus with magnetization and temperature is shown by the curves of Fig. 6. The points on these curves were calculated with Eqs. (2) and (3), and values of f_0 secured from smooth curves of the sort shown in Fig. 5.

Table II gives the variation with magnetization and temperature of the quantity $\Delta E/E$ defined by the formula, $\Delta E/E=(E_J-E_0)/E_0$. E_J and E_0 denote the values of Young's modulus when the value of the magnetization is, respectively, J and zero. E_0 is given as a function of the temperature in the third column of Table I.

The variation of the logarithmic decrement with magnetization and temperature is shown by the curves of Fig. 7.

TABLE I. *Variation of J_∞ with temperature.*

T	J_∞	$E_0\times10^{-11}$	T	J_∞	$E_0\times10^{-11}$
23.5	485	20.82	270	332	18.54
70.0	472	20.09	311	260	19.10
106	459	19.26	340	162	19.63
147	440	18.37	353	39	19.79
177	422	17.93	365	2	19.70
197	408	17.81	369	1	19.68
200	405	17.78	385	—	19.57
217	371	17.85	397	—	19.49

[6] This analysis, together with the specimen material itself, was furnished by the International Nickel Company.

Accuracy of the Measurements

Temperature

The Chromel-P *vs.* Alumel thermocouple was calibrated before and after the measurements against the melting points of ice, Sn, Pb and Zn. The two calibrations agreed to 0.25°C. The temperature variation *in the oven* over the region occupied by the specimen is less than 0.3°C. That along the specimen is, of course, considerably less. The temperature of the thermocouple in contact with the knife-edge (Fig. 1) agrees with that of the specimen to better than 0.1°C. Accordingly the error in the temperature measurement is not greater than 0.5°C.

Magnetic

The measurement (on the approximate ellipsoid) of the saturation magnetization is accurate to 1 percent. Values of J between zero and saturation are reliable to 2 percent, and errors arising from this uncertainty are reduced by the smoothing process represented by the curves of Fig. 5.

Elastic

The relation (Eq. (3)) between E and f_1 involves the length and density of the specimen cylinder at the temperature of observation. These are evaluated with accuracies of 0.02 and 0.05 percent, respectively, from measurements

TABLE II. $(E_J-E_0)/E_0$.

T \ J/J_∞	0.2	0.4	0.6	0.8	1.0
23.5	0.0040	0.015	0.035	0.055	0.067
70.0	.0065	.025	.052	.077	.096
106	.0088	.033	.071	.109	.131
147	.0109	.048	.094	.136	.170
177	.0084	.046	.106	.156	.186
197	.013	.053	.117	.163	.186
200	.013	.055	.116	.161	.188
217	.013	.053	.111	.152	.176
270	.0092	.039	.073	.098	.109
311	.0063	.023	.046	.055	.058
340	.0025	.0061	.011	.013	.016

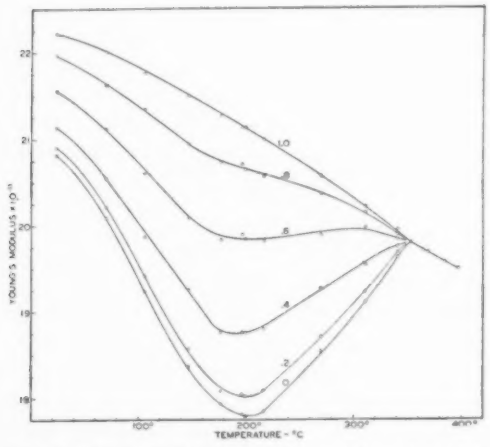

FIG. 6. Curves showing the variation of Young's modulus with magnetization and temperature in nickel. The numbers on the curves give the magnetization in fractions of the saturation value.

made at 30°C, together with values of the coefficient of thermal expansion of nickel reported by Williams.[7]

A possible source of error in the measurement of Young's modulus lies in the fact that about ten percent of the length of the specimen cylinder at each end is in a lower state of magnetization than that observed at its center. The maximum effect of the consequent elastic inhomogeneity on f_1 is readily obtained by an analysis similar to that which leads to Eq. (2). It follows that if the value of E over the end sections is assumed to be 0.9 the value over the central eight-tenths of the cylinder, then the resulting error in the calculated value of E is only 0.25 percent. This is merely a consequence of the fact that the fundamental frequency of free longitudinal vibration of a rod is principally determined by the *inertia* of its terminal parts and the *elasticity* of its central part. If the above-mentioned inhomogeneity occurred at the center of the cylinder the resulting error in E would be 4.2 percent.

The major part of the uncertainty in E arises from the flatness of the maxima and minima shown on the oscillograms when the decrement, δ, is large. The error thus introduced into the determination of f' and f'' can affect the calculated value of E by as much as 0.2 percent.

[7] Williams, Phys. Rev. **46**, 1011 (1934).

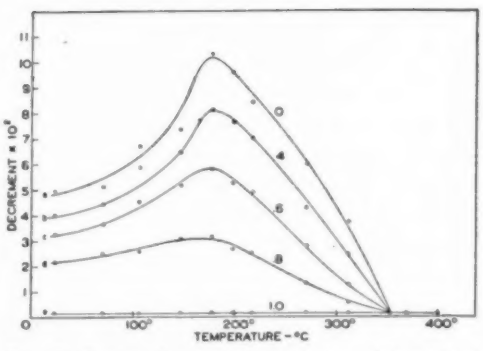

FIG. 7. Curves showing the variation of logarithmic decrement with magnetization and temperature in nickel. The numbers on the curves give the magnetization in fractions of the saturation value.

Finally, the reproducibility of the results is indicated by the observations at 197° and 200° as plotted in Fig. 6. The second set were taken a month later than the first. As a further test, the oscillator was demounted, disassembled, reassembled, and remounted, and a new set of data was taken with the specimen demagnetized and magnetized to saturation. The lowest and highest curves of Fig. 6 were reproduced with maximum accidental errors in E of 0.3 percent and 0.16 percent, respectively.

The values of δ obtained by the present method are reliable to 10 percent.

THEORETICAL DISCUSSION

The domain theory of ferromagnetism is based on the assumption that a ferromagnetic crystal is composed of a large number of regions, each of which is spontaneously magnetized to an intensity which is a function of the temperature alone. When the holomagnetization is zero these micromagnetizations are aligned in equal numbers along the various directions of "easy magnetization" of the crystal. The effect of a magnetizing field is, in the first instance, simply to alter this uniform distribution, so that a preponderant number of micromagnetizations lie in that direction of easy magnetization which most nearly coincides with the field. When this process is complete a further increase in the field strength produces a rotation of the micromagnetization of each domain into the direction of the field.

Each domain is deformed in a manner which

depends upon the direction of its magnetization. Consequently any alteration in the directional distribution of the micromagnetizations throughout the crystal is accompanied by a deformation of the crystal as a whole. When the alteration is produced, as above, by a magnetizing field alone, the resultant deformation constitutes the ordinary phenomenon of magnetostriction.

Now it is well known that the holomagnetization of a ferromagnetic body in a given magnetizing field is, in general, altered by the application of a stress, and furthermore, that *the magnitude of this alteration depends upon the magnetization*, being nil when the substance is magnetized to saturation. In terms of the domain theory this means that a given applied stress alters the distribution of the micromagnetizations, and hence the linear dimensions of the body, by an amount which depends upon the holomagnetization. This is the qualitative explanation of the phenomenon dealt with in this paper.

The problem is attacked quantitatively by Akulov,[1] who employs the analysis invented by Heisenberg[8] to resolve the simpler problem of single crystal magnetostriction. The procedure is simply to calculate the most probable distribution of the micromagnetizations for a given applied field and stress, subject to the conditions that the total number of domains and the quantity U are constant, where U is defined by the formula

$$U=-(H_1J_1+H_2J_2+H_3J_3)-F\lambda.$$

In this expression H_i and J_i are the components of the field and magnetization respectively, F is the applied force per unit area, and λ is that part of the change in length per unit length parallel to F which depends upon the distribution of micromagnetizations. The calculation yields the distribution in terms of H, J, F, and the magnetostrictive coefficient of a domain for a direction of easy magnetization. λ is evaluated in terms of the same quantities by summation over the array of domains, and from this the variation of the elastic modulus with magnetization. The behavior of a polycrystalline material is obtained by averaging over all directions in the crystal.

The calculation cannot be completed without approximation. Akulov obtains two formulae, one of which is valid when the applied field is small, and the other when the field is sufficiently large that the effect of stress on the distribution is nil. Thus, for a polycrystalline specimen of nickel in which the distribution of microcrystalline axes is random,

$$\frac{E_J-E_0}{E_0}=\frac{81}{35}\frac{\chi_0}{J_\infty^2}\lambda_{111}^2(J/J_\infty)^2, \tag{6}$$

provided J/J_∞ is small, while if $J=J_\infty$,

$$\frac{E_\infty-E_0}{E_0}=\frac{9\chi_0\lambda_{111}^2E_0/15J_\infty^2}{1-9\chi_0\lambda_{111}^2E_0/15J_\infty^2}, \tag{7}$$

where E_∞ denotes the value of Young's modulus when the material is magnetically saturated. In arriving at these expressions H has been expressed in terms of J by the formula, $J=\chi_0H$. Hence χ_0 is the initial magnetic susceptibility of a single crystal of nickel. λ_{111} is the saturation magnetostrictive coefficient for the direction of easy magnetization in the crystal. The measurements of Masiyama[9] give $\lambda_{111}=27\times10^{-6}$ and those of Becker and Kersten[10] give $\chi_0=20$, both at room temperature. These formulae and data will now be compared with the results of the present research.

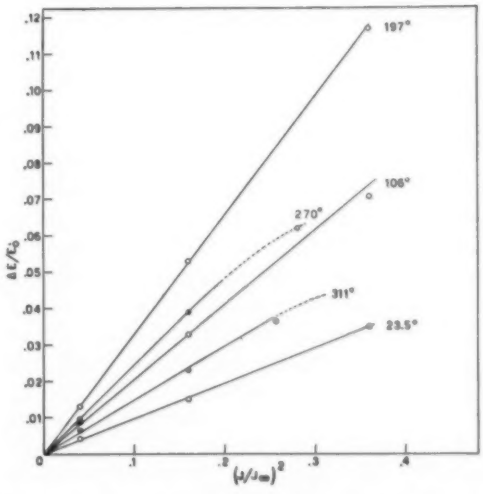

FIG. 8. $\Delta E/E_0$ is proportional to the square of the magnetization for values of J up to 0.4 saturation.

[8] Heisenberg, Zeits. f. Physik **69**, 287 (1931).

[9] Masiyama, Tohoku Imp. Univ. Sci. Rep. **17**, 945 (1928).

[10] Becker and Kersten, Zeits. f. Physik **64**, 660 (1930).

The straight lines shown in Fig. 8 indicate that, in accordance with Eq. (6), $(E_J-E_0)/E_0$ varies linearly with $(J/J_\infty)^2$ up to temperatures at least as high as 311°C, and for values of J/J_∞ as large as 0.4.

The calculated value of the coefficient of $(J/J_\infty)^2$ in Eq. (6) is 0.30. The observed value at 23.5°C is 0.10. The value of $(E_\infty-E_0)/E_0$ calculated from Eq. (7) is 0.085. The observed value at the same temperature is 0.067. An approximate test of the correctness of Eqs. (6) and (7), independent of the values of χ_0, λ_{111} and E can be obtained by noting that the value of the numerator on the right-hand side of Eq. (7) is only 0.078. Hence the ratio of this quantity to the coefficient of $(J/J_\infty)^2$ in Eq. (6) should equal 35/135, or 0.26, with an accuracy of 8.5 percent whatever the value of χ_0, λ_{111}, and E. The observed ratio is 0.67.

These discrepancies cannot be ascribed to a nonrandom distribution of microcrystals in the specimen. The possible values of the ratio noted in the preceding paragraph range from 0.20 for a (111) direction in a single crystal to 0.33 for a (110) direction. Nor can they be ascribed to the neglected effect of temperature, for it is observed that the ratio decreases with *increasing* temperature from the value 0.67 at 23.5°C to the value 0.39 at 311°C.

von Auwers[11] has investigated the ΔE effect in nickel at room temperature by a method different from that here employed. He obtains the values 0.30 and 0.43 for the ratio, as observed on specimens characterized, respectively, as "soft" and "very soft."

In conclusion, therefore, it is evident that, while the domain theory is probably essentially correct, the greatly simplified calculation of Akulov requires emendation of such nature as to alter at least the numerical coefficients in Eqs. (6) and (7).

The interpretation of the decrement measurements awaits the development of a theory of internal friction in ferromagnetic substances. It may be noted that the observed decrement of the magnetically saturated nickel (curve *e* of Fig. 7) is the same order of magnitude as that of nonferromagnetic materials.

The authors gratefully acknowledge their indebtedness to Mr. C. A. Crawford of the International Nickel Company for the specimen material and its analysis; to Mr. F. A. Nealon of the American Enameled Magnet Wire Company for the gift of the chromoxide covered wire; and to Professor William Campbell and Mr. Maurice Pinel of Columbia University for their assistance in the microscopic study of the polycrystalline specimen.

[11] von Auwers, Ann. d. Physik **17**, 83 (1933).

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Photoelectric Properties of Sodium Films on Aluminum

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Previous work has shown that thin films of potassium, rubidium, and caesium deposited on a silver surface give a maximum sensitivity when the thickness of the film is of the order of ten molecular layers or less. As the deposit continues the sensitivity decreases before reaching a constant value. Sodium films were deposited on aluminum, and it was found that the maximum sensitivity was not attained until the thickness of the film had reached a value of eighty molecular layers. The sensitivity was then found to remain constant for greater thicknesses. No detectable photo-current was observed until the film reached a thickness of five molecular layers. Spectral distribution curves were obtained and analyzed according to Fowler's theory. This yielded a value of 5150A for the threshold of the sodium film. These observations indicated that the threshold was the same for all thicknesses of film. Current-voltage curves were obtained for different thicknesses of film, and these were analyzed according to DuBridge's theory. These results also indicate that the work function of the various films is the same. It was concluded from these data that the work function of the freshly distilled aluminum on which the deposits were made was 4.08 volts. This gives a value of 3020A for the threshold of aluminum. It was found that the photoelectric current decreased immediately after forming a film, but that the decrease was much less for films greater than fifty molecular layers. It is suggested that this decrease results from the surface migration of the sodium atoms in forming aggregates.

Introduction

IT is well known that when only a small fraction of the surface of a tungsten or platinum plate is covered with either Cs, Rb, or K atoms, the work function of the composite surface is much less than that of the clean underlying metal. Langmuir and Kingdon,[1] and also Becker,[2] have taken the view that atoms may be adsorbed as ions on surfaces if the work function of the surface is greater than the ionization potential of the adsorbed atom. According to Becker's "ion-grid" theory, ions distributed here and there over the surface of a metal lower the work function of the composite surface. The criterion stated above, for the existence of adsorbed *ions*, must be taken only as a rough guide. Gurney[3] has pointed out, from quantum-mechanical considerations, that the criterion could be expected to apply only to single valence atoms (e.g., alkali metals) condensed on a surface. Experimental results for deposits of alkaline earth metals are in agreement with these views.[4] In terms of the picture discussed by Gurney, the criterion for the existence of an ion grid on the surface should be stated in terms of probability. If the work function of the underlying surface is greater than the ionization potential of the adsorbed atom, the *probability* of its being adsorbed on the surface as an *ion* is quite high. On the basis of this theory, there is a *finite* probability for the existence of adsorbed ions on the surface even though the ionization potential of the deposited atoms is equal to or even slightly higher than the work function of the underlying metal. The probability would be expected to decrease to a very small value if the ionization potential of the atom were much greater than the work function of the surface.

It was the purpose of this investigation to choose a combination such that the ionization potential of the deposited atoms was considerably higher than the work function of the underlying metal. It was desirable also to choose a combination that would give a photoelectric effect with visible light. Sodium films deposited on aluminum satisfied these conditions.

Brady[5] reported in studies of the photoelectric properties of K, Rb, and Cs films deposited on silver that the maximum sensitivity was reached when the calculated thickness of the film was in the order of ten molecular layers or less (depending on the frequency of the exciting light). In the same report a curve was shown for sodium deposited on tungsten and the maximum sensitivity was not reached until the thickness of the film was well over one hundred molecular layers.

Fig. 1 is an unpublished curve from Brady's data and it is interesting to contrast this with Fig. 2.

Experimental Procedure

The photoelectric cell was almost identical to that used in a previously reported experiment.[6] Likewise, the same procedure was used for evacuating the cell. After a thorough outgassing treatment, the cell was sealed off from the pumps. During the course of an experiment, the charcoal trap attached to the cell was immersed in liquid air. This reduced the pressure within the cell to less than 10^{-8} mm of Hg as registered by the ionization gauge. The sodium was outgassed by repeated distillation before being driven into the lower part of the photoelectric cell. The aluminum which formed the underlying surface was distilled from 30 mil tungsten spirals.

All photoelectric studies were made *immediately* after depositing a fresh coat of aluminum on the inside surface of the cell. This was done to insure an outgassed surface on which to deposit the sodium films.

A mercury arc with suitable filters was used as a light source in most of the experiments. The spectral distribution curves were obtained by using a tungsten filament lamp in conjunction with a double prism monochromator of the van Cittert type.

As in the previous work,[6] a monomolecular layer is defined on the assumption that the atomic spacing for the sodium atoms is the same in the film as in a solid mass of the metal. It is assumed, also, that the underlying surface is perfectly smooth. On these assumptions, a mono-

[1] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107**, 61 (1925).
[2] J. A. Becker, Phys. Rev. **28**, 341 (1926).
[3] R. W. Gurney, Phys. Rev. **47**, 479 (1935).
[4] J. A. Becker, Trans. Faraday Soc. **28**, 155 (1932).
[5] J. J. Brady, Phys. Rev. **41**, 613 (1932).
[6] J. J. Brady, Phys. Rev. **46**, 768 (1934).

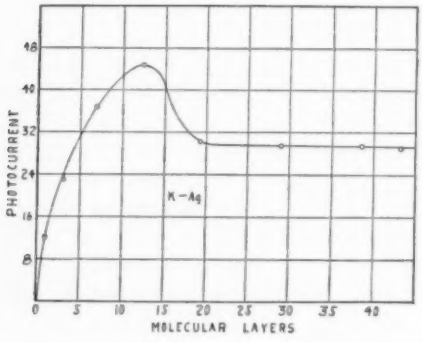

FIG. 1. Variation of photo-current with the thickness of a potassium film deposited on silver (after Brady).

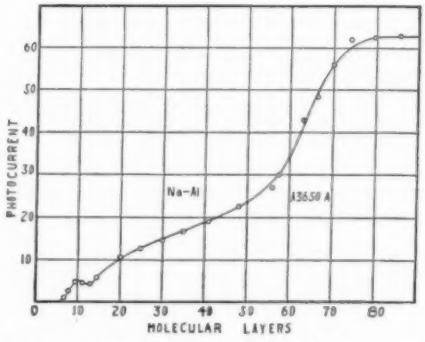

FIG. 2. Variation of photo-current with the thickness of a sodium film deposited on aluminum.

molecular layer of sodium is equivalent to a deposit of 8.7×10^{14} atoms/cm^2.

RESULTS

Fig. 2 shows a typical curve for the variation of photo-current with the thickness of the film. No photo-current was detected before the deposition of the sodium, even in the presence of a very intense white light. The Pyrex window of the cell was effective in cutting out the shorter wave-lengths which would cause the aluminum to emit photoelectrons. The photo-current from the sodium film became detectable only when the thickness of the film had reached a value in the order of 5 molecular layers, even though an intense source of white light was used. Beyond this thickness of the film, the sensitivity increased rapidly. The mercury arc with filters to isolate the 3650A band of wave-lengths was then substituted for the white light source.

An accelerating potential of twelve volts was found sufficient to saturate the photo-current in all cases and was employed in obtaining the data for Fig. 2.

As the thickness of the film increased, the photoelectric sensitivity increased rapidly until the deposit of sodium reached a value of approximately 10 molecular layers. From 10 molecular layers to 50 layers, the increase in sensitivity was not as rapid as in the earlier deposits. The sensitivity then increased more rapidly for thicknesses of film greater than 50 molecular layers, until a deposit of approximately 80 layers was reached. Beyond this, the photo-current remained practically constant for increasing thickness of film.

Spectral distribution curves were obtained for several films of different thicknesses—from fifteen to one hundred molecular layers. Although the sensitivity of the thin films was not great enough to investigate the curves as far toward the long wave-lengths as in the case of the thicker films, the results gave *no* indication of a change in threshold (or work function) in going from one thickness of film to another.

A spectral distribution curve for a one hundred molecular layer film is shown in Fig. 3. The ordinates give the photo-current per unit light intensity in arbitrary units. The slits of the monochromator had to be opened to a considerable width in order to obtain enough light intensity to give an appreciable photoelectric effect. This means that a rather wide wave-length band (approximately 200A) was used. Fig. 4 shows how these observations fit the theoretical curve of Fowler.[7] The points obtained for the short wave-lengths fit the theoretical curve very well, but those obtained for the long wave-lengths show a wide divergence from the theory. The horizontal shift of the experimental curves, as plotted according to the method outlined by Fowler, to make it coincide with the theoretical curve, indicated a value of 5150A for the true threshold of the sodium film. It was assumed that the divergence of the points taken for the long wave-lengths from the theoretical curve

[7] Hughes and DuBridge, *Photoelectric Phenomena* (1932), p. 248.

was due to the wide band of wave-lengths from the monochromator, with perhaps some accompanying scattered light of short wave-length. The dotted curve in Fig. 3 was obtained by choosing values of the photo-current which would cause the longer wave-length points to fit the theoretical analysis curve. The contact potential between the sodium film and the aluminum collecting surface may be obtained from the value of the threshold of the sodium film and data taken from the current-voltage curves, Fig. 5. These curves cut the applied potential axis at approximately 0.7 volt. The energy in the exciting light (3650A) is 3.38 volts. The energy of the fastest moving photoelectron is the difference between 3.38 volts and the work function of the sodium film. The threshold, 5150A, corresponds to a work function of 2.40 volts. The energy of the fastest photoelectron is then (3.38−2.40) 0.98 volt. This value when added to the 0.7 volt gives the contact difference of potential between the two surfaces, or (0.7 +0.98) 1.68 volts. The threshold of the aluminum was then determined by adding the contact potential to the threshold of the sodium film, or (1.68+2.40) 4.08 volts. This gives, approximately, 3020A as the threshold of aluminum. This value is considerably lower than any reported by previous experimenters.[8]

Fig. 6 shows the theoretical analysis of the data obtained from the current-voltage curves. Because the results from the films of different thicknesses agree near the "tail" of the current-voltage curves, only the results for the thick film (100 molecular layers) are shown. When the values of the saturation current for the different films are reduced to a common level, the "tails" of the curves coincide for every thickness of film. The current-voltage curves for two films, as shown in Fig. 5, illustrate this point.

The data for the full line curve in Fig. 6 were taken from a paper by Roehr.[9] The experimental results were plotted in the form log (I/x) against x as outlined in DuBridge's theory.[10] The horizontal shift gave a value of 0.96 volt as the maximum energy of the photoelectrons at absolute zero. This compares quite closely with the 0.98 volt as determined from the analysis according to Fowler's theory.

Figs. 7, 8, 9, and 10 indicate the way the photoelectric current varies immediately after the heat is removed from the sodium reservoir. The zero point on the time axis represents the instant the photo-current began to decrease after the removal of the heater. Figs. 7 and 8 indicate that the decrease is about the same for films which are less than 50 molecular layers. Those greater than 50 layers do not show as rapid a decrease in photo-current after a deposit is made. It is interesting to note that Andrade and Martindale[11] have presented evidence that the films they were studying began to form a definite crystal lattice after the thickness had reached 50

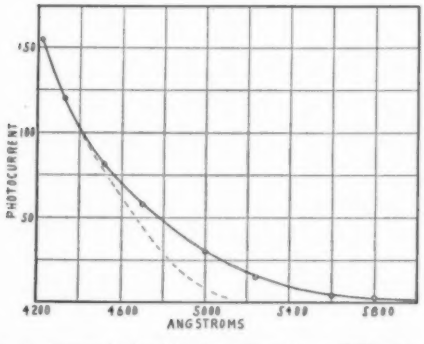

FIG. 3. Spectral distribution curve for a 100 molecular layer sodium film. The dotted curve represents the curve corrected for a wide wave-length band.

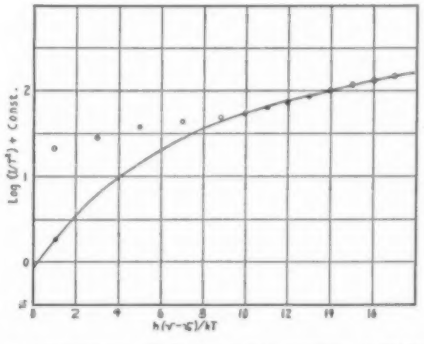

FIG. 4. Theoretical analysis of the spectral distribution curve according to Fowler's theory.

[8] Reference 7, p. 74.

[9] W. W. Roehr, Phys. Rev. **44**, 866 (1933).
[10] L. A. DuBridge, Phys. Rev. **43**, 727 (1933).
[11] Andrade and Martindale, Phil. Trans. Roy. Soc. **235**, 69 (1935).

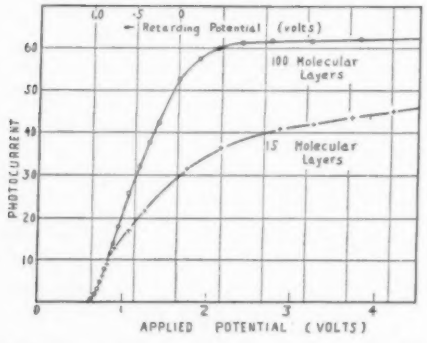

FIG. 5. Current-voltage curves for two different thicknesses of the sodium film. The contact potential is 1.68 volts.

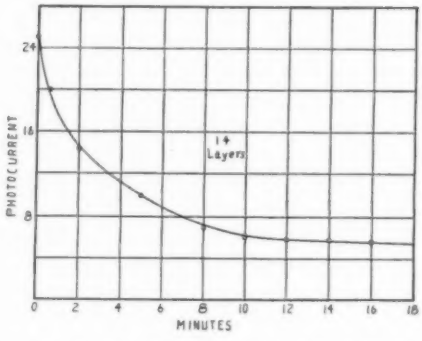

FIG. 7. Decrease in photo-current with time after forming a deposit of 14 molecular layers.

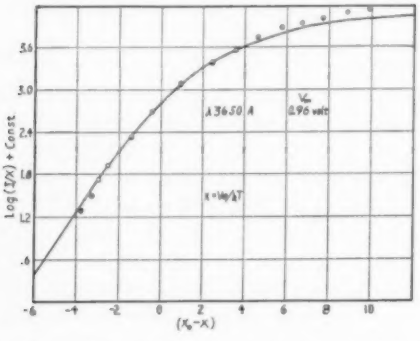

FIG. 6. Theoretical analysis of the current-voltage curves according to DuBridge's theory.

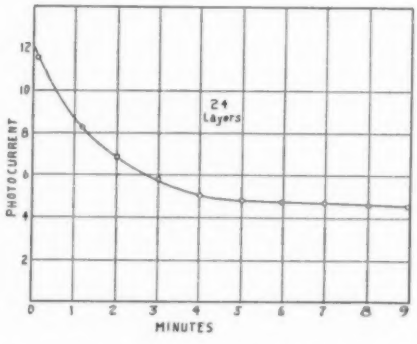

FIG. 8. Decrease in photo-current with time after a deposit of 24 molecular layers.

molecular layers. The earlier deposits were aggregates without a crystalline structure.

The decrease in photo-current for the early deposits is most likely due to the surface motion of the deposited sodium atoms. This results in the formation of aggregates, which, in turn, lead to a reduction in the effective area of the sodium which is exposed to the light.

Bosworth[12] has shown, in his studies of sodium on tungsten, that the decay in the photoelectric current is due to a diffusion of the sodium atoms into the tungsten. After 10^{17} atoms/cm^2 have been deposited the tungsten becomes saturated and the photo-current no longer decreases with time. Because of the final constant value of the photo-current after standing a short time it is concluded that no such phenomenon occurs in our experiment.

[12] R. C. L. Bosworth, Proc. Roy. Soc. **A150**, 58 (1935).

CONCLUSION

The essential differences between the photoelectric properties of Cs, Rb, or K films on silver and the films of sodium on aluminum are:

1. In the former case, there is a strong photoelectric effect when the films are less than one molecular layer thick, while in the latter case, the effect cannot be detected even with a strong light until the thickness is in the order of 5 molecular layers.

2. The other films show a maximum sensitivity when the film thickness is in the order of a few molecular layers whereas the sodium films on aluminum do not reach their maximum sensitivity until the thickness is in the order of 80 molecular layers.

3. After passing through a maximum sensitivity, the other films show a decrease in photo-current in going to greater film thicknesses. The sodium-on-aluminum films show no decrease in photo-current with increase in film thickness after the thickness for maximum sensitivity had been passed.

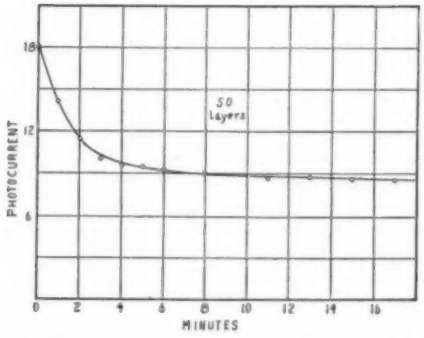

FIG. 9. Decrease in photo-current with time after a deposit of 50 molecular layers.

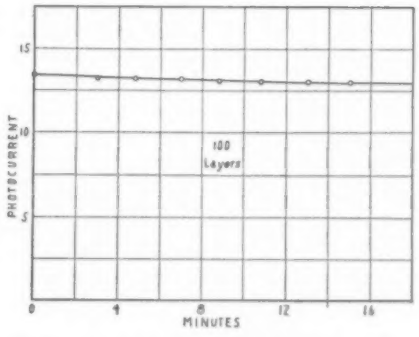

FIG. 10. Decrease in photo-current with time after a deposit of 100 molecular layers.

The outstanding difference from the theoretical standpoint is this—in one case the work function of the underlying surface is greater than the ionization potential of the alkali metal, while in the other case the work function is less. Ives and Briggs[13] have shown that the electrons originate in the underlying metal for the early stages of film development in the case of sodium on silver. As the thickness of the film increases, more and more electrons originate in the alkali metal.

Because of the comparatively small difference between the ionization potential of sodium and the work function of silver, there is a certain probability that sodium ions will exist on the surface of the silver during the early stages of deposition. These ions allow the electrons in the silver to be released by visible light by reducing the work function of the silver. In the case of sodium on aluminum, the difference between the ionization potential and work function is much greater and the probability of *adsorbed ions* being deposited is much less than in the above case. The photoelectrons must then originate solely in the sodium film. As a result, the sodium must be allowed to build up to a relatively thick deposit in order to present an appreciable volume for the absorption of light before a detectable photoelectric effect could be expected.

The evidence from the spectral distribution curves and also the current-voltage curves indicates that the change of sensitivity with the thickness of the film is *not* due to a change of the work function of the surface. This would lead one to conclude that the change in sensitivity is due to the change in the amount of light absorbed in the sodium film as its thickness is changed. One need not conclude, however, that the photoelectrons in a thick film come from a depth of 80 molecular layers. The monomolecular layer was defined on the basis of a perfectly smooth underlying surface. Because of the method used in evaporating the aluminum, the underlying surface was undoubtedly far from being perfectly smooth. The actual surface may be much larger than the apparent surface. This point is discussed by De Boer.[14]

The senior author (J. J. B.) wishes to express his indebtedness to the Physics Department of the University of California for the loan of the monochromator used in this research.

[13] Ives and Briggs, Phys. Rev. **40**, 802 (1932).

[14] J. H. De Boer, *Electron Emission and Adsorption Phenomena* (1935), p. 133.

Wave Functions for $1s2s\ ^1S$ Helium

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The $1s2s\ ^1S$ state of He has been treated with a variant of Hylleraas' variational method, and a wave function has been determined which gives an error of only 0.005 ev in the energy of the system. The properties of desirable functions for use in this method are discussed. Wave functions of the Hartree and Fock types, and a more flexible function not involving r_{12}, are also determined by simple variational processes. The properties of the resulting functions are compared, and are discussed in the light of the polarization method of Hylleraas and Bethe, properly applicable to more highly excited states. The computations by the polarization method have been extended, and the results are compared with those given by the variational procedure.

INTRODUCTION

ONE of the most interesting of the singly excited states of He, as well as one of the most difficult to treat, is the $2s$ state of parahelium. The difficulty arises from the fact that in the treatment of the moderately excited S states of He, methods of approximation which are satisfactory elsewhere tend to break down. This forces one to rely on variational methods, which are in general not so easily applied to excited states as to ground states. The best previously found wave function for this state is that of Hylleraas and Undheim.[1] The agreement of their energy with the experimental value is markedly poorer than that given by the Hylleraas method for the normal or the $2s$ *ortho* state of the atom.[2] In the study of this state of He, as a preliminary to the treatment of the ground state of lithium, we have therefore attempted to extend and improve the method by increasing its flexibility with respect to the radial coordinates, introducing two modifications. The first and more important consists of the use of two sets of terms with different values of the exponent applying to the "outer" electron. This corresponds to the work of Wilson[3] and others who have constructed single orbitals for excited electrons by superposing terms with different exponentials, finding that only a very few terms are required. The second consists in forming the wave function as a sum of terms which differ somewhat in form from those used by Hylleraas and Undheim, which may be constructed as sums and differences of our terms. Use of these terms somewhat mars the elegance of the mathematical treatment, but contributes to the clarity of the physical picture. It also tends to reduce the number of terms needed to attain a given accuracy in the treatment of the system.

Having thus produced a considerable increase in the accuracy with which this state can be treated we have chosen it as one suitable for a detailed consideration of the way in which atomic wave functions vary with the distance between the electrons, and for a comparison of the successes obtained by various simpler methods of attacking the problem. For this purpose it is particularly satisfactory in that the relation of the electrons is similar to that obtaining in interesting atoms such as Li, Na, etc., while this system is much easier to treat accurately.

FORM OF WAVE FUNCTIONS

The wave functions employed were of the form $\psi=\sum_{mnp}C_{mnp}[mnp]$, where $[m,\ n,\ p]=(\kappa^3/4\pi)\{e^{-\nu\kappa r_1}(\kappa r_1)^m e^{-\delta\kappa r_2}(\kappa r_2)^n+e^{-\nu\kappa r_2}(\kappa r_2)^m e^{-\delta\kappa r_1}(\kappa r_1)^n\}(\kappa r_{12})^p$. κ is here a scale constant, δ and ν are parameters, and the distances which define a configuration are represented in the usual way. Other terms were also introduced, which we designate by $[m^*np]$, in which the * is not an adjunct of the m, but indicates that in these terms ν has been replaced by another parameter, ν^*. While the best value of κ could easily be determined during the final variation, we desired to base all our computations upon a single set of tables computed for fixed values of

[1] E. A. Hylleraas and B. Undheim, Zeits. f. Physik **65**, 759 (1930).
[2] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).
[3] E. B. Wilson, J. Chem. Phys. **1**, 210 (1933).

the parameters δ, ν, ν^*, and after experimenting with some simple functions (of the type later called $F\Phi$), selected the following as suitable: $\delta=2$, $\nu=0.55$, $\nu^*=1$. Thus, δ is characteristic of a one-quantum orbital about the bare nucleus, ν corresponds to a two-quantum orbital governed by a highly shielded nucleus, and the star terms are useful in dealing with the region in the atom where the outer electron makes a close approach to the nucleus, penetrating a region where the shielding is less effective.

One advantage of the form chosen for terms in our wave function appears in the ease with which orbital functions can be represented. Thus, such a function as that employed by Zener[4] is simply $[100]+c[000]$. The terms used by Hylleraas and Undheim are linear combinations of ours, $[100]\pm[010]$, $[200]\pm2[110]+[020]$, $[200]-[020]$, etc.; it would require three of these to give the Zener function. This advantage is only partially lost in going to more general functions, for the helpful terms are those which are not too different from the ones occurring in the product functions. Our method enables these terms to be introduced by themselves, whereas in Hylleraas and Undheim's functions the helpful terms are linked with harmful ones, which can be removed only by using additional terms in order to cancel them out. For example, in constructing our best function, we can do as well by the inclusion of $[200]$ and $[110]$ alone as with the last three of the above combination terms; the term $[020]$ is harmful and must be eliminated.

The form of trial function adopted enabled us to determine analytical approximations to several simplified functions as well as to the correct function, permitting various interesting comparisons. The four functions which our approximations approach as limits are:

The Hartree function ($H\Phi$); the best function expressible in the form $K(r_1)\times L(r_2)$, where $K(r)$ and $L(r)$ are single-electron functions of the general character of $1s$ and $2s$ orbitals.

The Fock function ($F\Phi$); the best function which can be expressed as $K(r_1)\times L(r_2)+K(r_2)\times L(r_1)$, where $K(r)$ and $L(r)$ are similar to but not identical with those occurring in the $H\Phi$.

The Best Radial function ($R\Phi$); the best function of any form containing only r_1 and r_2, which must enter symmetrically.

The Correct function ($C\Phi$); a function of r_1, r_2, and r_{12}, the first two entering symmetrically.

(The above abbreviations will be applied also to our analytical approximations where no confusion will result.)

It must be clearly understood that these four limiting functions have a definite existence independent of the method used to approximate them. Thus $R\Phi$ is the exact solution of a differential equation obtained from the Schrödinger equation upon replacing $1/r_{12}$ at each point in configuration-space by its mean value over all points having the same values of r_1 and r_2, i.e., by $1/g_{12}$ where g_{12} is the greater of r_1 and r_2. There results an equation involving only r_1 and r_2, but it cannot be separated and solved by a product of single-electron functions. The equations solved by $F\Phi$ and $H\Phi$ are sufficiently well known.

In the ensuing discussion we shall distinguish between two forms of atomic wave function constructed from the Hartree single orbitals. The first, which we shall designate $H_0\Phi$, is that already described, which neglects the requirement of symmetry in electron coordinates. The second, $H_x\Phi$, meets this requirement by the addition of exchange terms: it has thus the same form as $F\Phi$, but the coefficients are those determined by minimizing the energy of $H_0\Phi$. To find the energy of $H_x\Phi$ requires an additional computation, using these coefficients explicitly.

In using the variational method to find approximations for the various types of limiting function, we have simply to observe certain restrictions on the character of the terms used or the way in which they enter. The product functions $H\Phi$ and $F\Phi$ must have the form

$$\sum_m\sum_n c_m c_n'[m, n, 0]+\sum_m\sum_n c_m^* c_n'[m^*, n, 0]$$

corresponding to $K(r)=e^{-\delta r}\sum c_n' r^n$, $L(r)=e^{-\nu r}\sum c_m r^m+e^{-\nu^* r}\sum c_m^* r^{m^*}$, (taking $\kappa=1$). In determining $H\Phi$, of course, the exchange terms have to be omitted from the definitions of the functions and from the matrix formulas. Corresponding to the conventional way of determining these functions, we first assume that $K(r)=e^{-2r}$, the He^+ $1s$ function; we thus determine preliminary values of the c and c^* by variation among all terms having $n=0$, $p=0$. The next stage of approximation improves $K(r)$, determining the c' by a variation among individual terms each in the form $\sum_m\{c_m[m, n, 0]+c_m^*[m^*, n, 0]\}$. The c and c^* can then be readjusted if necessary,

[4] C. Zener, Phys. Rev. **36**, 51 (1930).

holding the c' constant, and so on until self-consistent results are reached. $R\Phi$ is obtained by an unrestricted variation among all terms having $p=0$; the removal of this specialization gives $C\Phi$.

In none of these variations (except that determining the $K(r)$ factor in the product functions $H\Phi$ and $F\Phi$) were we seeking an absolute minimum value of the energy parameter. Hylleraas and Undheim have shown, however, that the second root of the secular equation can never lie lower than the second characteristic energy value of the problem, and approaches that value as a limit as the terms in the series are improved, even though the lowest root may be at the same time a very poor approximation to the lowest energy value. The only precaution in using the method is, therefore, to be sure that one has the proper root.

Introduction of r_{12}

There has been considerable experimentation to determine the most practical way of introducing r_{12} into the wave function. It will not do, (as Hylleraas and Undheim point out) merely to multiply a function of the $R\Phi$ type by $(1+cr_{12})$. Inspection of Table I will show that we find no tendency for the coefficients of the terms $[m, n, 1]$ to be proportional to those of the corresponding terms $[m, n, 0]$, a result likewise noticed by Hylleraas and Undheim. A possible guide to the selection of r_{12} terms can be derived by applying a method due to Hassé and Lennard-Jones.[5] We regard $R\Phi$ as the solution of an unperturbed equation, and introduce as a perturbation the quantity $1/r_{12}-1/g_{12}$. Then the Hassé approximation to $C\varphi$ is

$$R\Phi\{1+c[1/r_{12}-1/g_{12}]\},$$

c being a constant to be determined by variation. The energy corresponding to this function is not integrable over small r_{12}, but this is a defect in the approximation and not a property of the function which we desire to represent. Upon multiplication of the perturbation term by r_{12}/g_{12} we remove this defect and obtain an expression which is but little different from the Hassé approximation in regions where one r is much greater than the other, these regions being those where the approximation itself is valid, and simultaneously those in which the factor $R\Phi$ takes on its largest values. In a wave function for an excited atom, it is a small approximation to replace g_{12} by r_1 and r_2, respectively, in the terms in which electron 1 and electron 2 are assigned the more diffuse distribution. From each term $[m, n, 0]$ of $R\Phi$ we thus derive $[m, n, 0]+c\{[m-1, n, 0]-[m-2, n, 1]\}$. The argument not being rigorous, we can in general get the best results by introducing the new terms with free coefficients to be determined by variation, rather than adhering to the relations between the coefficients which the Hassé approximation prescribes. Nevertheless we should expect definite cooperation between the terms which in the theory occur in pairs; each term in r_{12} may be most helpful only when a corresponding term, which behaves in nearly the same way for large r, is included in the series to be varied.

Terms suggested by this reasoning cannot be used for $m<2$, for they would not be properly integrable. It may therefore be necessary to employ, say, the terms $[m, n, 0]$ and $[m-1, n, 1]$. Moreover, terms such as $[m+1^*, n, 0]$ and $[m^*, n, 1]$, are always available, and may to a certain extent take the place of $[m-1, n, 0]$ and $[m-2, n, 1]$, since both sets have the common feature of representing more compact distributions than the term $[m, n, 0]$ from which they are derived. We believe that this explains the fact that the introduction of star terms is more

TABLE I. *Computed wave functions and energies.*

FUNCTION	$H\Phi$	$H_x\Phi$	$F\Phi$	$R\Phi$	$C\Phi$
Energy, in $2Rh$		−2.13915	−2.14309	−2.14407	−2.14580
Energy error (ev)		0.185	0.078	0.052	0.005
		1.00	1.00	1.05	1.05
$\frac{\kappa}{y^2}$ per electron	14.447	14.223	16.756	16.485	16.036
COEFFICIENTS OF TERMS IN NORMALIZED FUNCTIONS					
(000)		25.21939	8.41368	4.88925	
(100)		−6.32769	−2.75611	−0.02948	0.35368
(010)			−0.00725	−.85415	−.69387
(110)			.00237	.23488	.14042
(200)		0.28620	.05770	.09866	.12251
(020)			.03635	.03271	
(210)			−.00005		
(120)			−.01191		
(220)			.00025		
(0*00)		−20.80546	−5.66385	−7.17757	−2.30134
(1*00)		−7.90329	−2.14445	−2.26128	0.47626
(0*10)			.00488	1.39627	1.08184
(1*10)			.00185		
(0*20)			−.02447		
(1*20)			−.00926		
(001)					0.63432
(101)					−.08422
(011)					.07633
(0*01)					−1.21923

[5] J. E. Lennard-Jones, Proc. Roy. Soc. **A129**, 598 (1930); H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930).

helpful in constructing the function with r_{12} than when the terms with r_{12} are omitted.

The importance of a given term is by no means indicated by the magnitude of its coefficient in the series, partly because the terms as we define them are very differently normalized, and partly because it may happen that two fairly similar terms enter with large coefficients of opposite sign, the net result being a very small alteration of the function which might be ignored without serious effects. (In such a case it is not worth while to consider the corresponding terms in r_{12}.) A principal and indispensable term (as indicated by its effect on the computed energy) may thus have a relatively small coefficient, and serve as the basis for the construction of useful r_{12} terms, while other terms with larger coefficients are ignored for this purpose.

Evaluation of Matrix Components

The required matrix elements can all be found in terms of the integrals

$$J(f,\ g,\ h/\alpha,\ \beta)=(1/16\pi^2)\int dV r_1^f e^{-\alpha r_1} r_2^g e^{-\beta r_2} r_{12}^h.$$

$$J(m,\ n,\ -1)=V_{m+2,\ n+1}(\alpha,\beta)+V_{n+2,\ m+1}(\beta,\alpha),$$

$$J(m,\ n,\ 0)=V_{m+2,\ n+2}(\alpha,\beta)+V_{n+2,\ m+2}(\beta,\alpha)$$
$$=A_{m+2}(\alpha)\times A_{n+2}(\beta),$$

$$J(m,\ n,\ 1)=V_{m+2,\ n+3}(\alpha,\beta)+V_{n+2,\ m+3}(\beta,\alpha)$$
$$+\tfrac{1}{3}[V_{m+4,\ n+1}(\alpha,\beta)+V_{n+4,\ m+1}(\beta,\alpha)],$$

$$J(m,\ n,\ 2)=V_{m+2,\ n+4}(\alpha,\beta)+V_{n+2,\ m+4}(\beta,\alpha)$$
$$+V_{m+4,\ n+2}(\alpha,\beta)+V_{n+4,\ m+2}(\beta,\alpha)$$
$$=A_{m+2}(\alpha)\times A_{n+4}(\beta)+A_{m+4}(\alpha)\times A_{n+2}(\beta).$$

Here $$A_n(\alpha)=\int_0^\infty e^{-\alpha\lambda}\lambda^n d\lambda$$

and $$V_{nm}(\alpha,\beta)=\int_0^\infty \lambda^n e^{-\alpha\lambda}d\lambda\int_\lambda^\infty \mu^m e^{-\beta\mu}d\mu.$$

The latter quantities are conveniently computed by using formulas given by the writers.[6]

Consider two terms $[m, n, p]$ and $[m', n', p']$; as either or both may carry stars we must distinguish between the possibly different values ν and ν' which occur, whereas κ and δ must be the same in both terms. Between these terms the matrix element of unity is

$$2J(m+m',\ n+n',\ p+p'/\nu+\nu',\ 2\delta)$$
$$+2J(m+n',\ n+m',\ p+p'/\nu+\delta,\ \nu'+\delta);$$

which may be abbreviated to $2J(000)+2J'(000)$, the general scheme of abbreviation being such that $J(a, b, c)$ stands for $J(m+m'+a,\ n+n'+b,\ p+p'+c/\nu+\nu',\ 2\delta)$ and $J'(a, b, c)$ is similarly formed from the "exchange" term. The matrix element of the energy, in units of $2R_\infty h$, is the sum of two terms involving J and J', respectively, with identical coefficients as follows:

$$\kappa^2\{-(\nu^2+\delta^2)J(000)+\nu(2m+p+2)J(-100)$$
$$-m(m+1+p)J(-200)+\delta(2n+p+2)J(0-10)$$
$$-n(n+1+p)J(0-20)+p[\{-2(p+1)-m-n\}$$
$$\times J(00-2)+\nu J(10-2)-\nu J(-12-2)$$
$$+mJ(-22-2)+\delta J(01-2)-\delta J(2-1-2)$$
$$+nJ(2-2-2)]\}+2\kappa\{J(00-1)-2J(0-10)$$
$$-2J(-100)\}.$$

It will be noted that these coefficients depend only on the first of the two combining terms. A symmetrical formula could of course be obtained; but the unsymmetrical form has the advantage of permitting a check against the alternative calculation in which the terms are interchanged.

Results

In Table I will be found the wave functions and energies obtained in our best computations with functions of the various types.

The energies stated are those for the fixed nucleus problem, in units of $2R_\infty h=27.074$ ev. Hylleraas[2] has shown that, to the approximation in which one can neglect the dependence of the wave functions on r_{12}, these numbers also give the energies of the corresponding approximate solutions of the free nucleus problem in units of $2R_{\mathrm{He}}h=27.070$ ev. Bethe[7] has shown that for the ground state the correction for dependence on r_{12} of the function is a fifth of that above. In the present computations this further correction has been neglected, for the dependence of $C\Phi$ on r_{12} is much less important; the error in the energy arising from neglect of r_{12} terms is less than a tenth of that found for the ground state. The errors given in Table I are then differences between the corrected energies and the observed energy of the system.

[6] H. M. James and A. S. Coolidge, Phys. Rev. **49**, 688 (1936).

[7] H. Bethe, *Handbuch der Physik*, Vol. 24/1.

A discussion of these results falls naturally into two parts; in the first we are concerned with the reliability of the approximations which the variation method yields, taking the four limiting functions and their corresponding energies as standards of perfection, while in the second it is these limiting functions themselves which interest us, and which we regard as sufficiently well represented by our approximations.

Accuracy of Results Obtained by the Variational Procedure

Hylleraas and Undheim estimate that the limiting energy obtainable by a function of the radial type is -2.14400. We have barely surpassed this, reaching -2.14407. There appears to be no calculation of the function itself available for comparison. This is also true of the correct function.

As measured against experiment, the error in our approximation to the energy of $C\Phi$ is only about one-sixth of that associated with the six-term function of Hylleraas and Undheim, the best previously available. The essential difference between the two functions is the addition of the ν^* terms, to be discussed later. Other terms were introduced, but discarded as being of no value. The explorations made were, however, not sufficiently extensive to permit an accurate estimate of the convergence limit, in accordance with the procedure outlined elsewhere.[8]

In the case of the Hartree function, it is possible to make a direct comparison between the results of the variation method and those obtained by accurate numerical integration by Wilson and Lindsay[9] at the first stage of the calculation, in which the $1s$ orbital is taken as e^{-2r}. The energy parameter ϵ for the $2s$ orbital we find to be $\epsilon_2 = 0.3054$, and Wilson informs us that they obtained precisely the same value, this proving the effectiveness of our variational procedure. In view of the existence of their complete solution, we have not carried out any further stages of approximation. In any case, the differences between our function and their final one are so small that we shall use our function in the following discussions.

The value given by Wilson[10] for the energy of this state is, however, very different from ours, his computed ionization energy being less than that observed by 0.81 ev, while ours is in error by only 0.184 ev. Wilson calculated the energy of the atom by introducing into the formulas of Slater[11] values which he obtained for the integrals using his Hartree orbitals. In doing so he neglected the nonorthogonality of his orbitals; his value is accordingly not the energy associated with a wave function constructed from the Hartree orbitals, as ours is, and his computed ionization energy is not comparable with other results of the Hartree method.

Our approximate Fock function was obtained as a second approximation, varying each factor once. A further variation gave no appreciable change in the $2s$ orbital; this function thus represents the best approximation to the Fock function obtainable with the terms included. It may be compared with that computed by Hylleraas,[12] likewise by the variation method, but with a different series, and without varying the $1s$ orbital. Taking $\nu = 0.5$, he finds with the three terms $[m00]$, $m = 0, 1, 2$, the energy -2.14275, which sinks to -2.14294 upon inclusion of two more terms of the same series. Judging by the smallness of the improvement given by the fifth term, he accepts this value as substantially the limit of convergence. With the same three terms as Hylleraas (but with $\nu = 0.55$) we find the energy -2.14285; putting $[0^*00]$ in place of $[200]$ gives us -2.14293, illustrating the usefulness of the star terms. With $[200]$ and $[1^*00]$ in addition, we reached the value -2.14307, appreciably lower than Hylleraas' apparent convergence limit. The value given in Table I, -2.14309, shows the minute improvement resulting from variation of the $1s$ orbital, and justifies Hylleraas in neglecting this step. Comparison of numerical values of his $2s$ orbital with ours shows typical discrepancies of one or two percent; in view of the lower energy, we believe our result is superior. Our complete atomic function should be more reliable than that of Hylleraas also because we have improved the $1s$ factor.

[8] H. M. James, A. S. Coolidge and R. D. Present, J. Chem. Phys. **4**, 187 (1936).
[9] W. S. Wilson and R. B. Lindsay, Phys. Rev. **47**, 681 (1935).
[10] W. S. Wilson, Phys. Rev. **48**, 536 (1935).
[11] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[12] E. A. Hylleraas, Zeits. f. Physik **83**, 739 (1933).

Comparative Accuracy of the Methods of Approximation

The functions $H_z\Phi$ to $C\Phi$ which we have obtained may be considered as successive steps in the determination of an accurate function, in which approximations are successively removed. The approximations in $H_z\Phi$ consist of neglect of exchange in determining the function and failure to give a detailed treatment of the interelectronic repulsion. In $F\Phi$ the first of these is removed, while $R\Phi$ and $C\Phi$ represent two steps in taking better account of the electronic interaction. For comparison with our results on this state there appear in Table II certain corresponding values for the ground states of He and Be.

The exchange effects in $1s2s\ ^1S$ He and $(1s)^2(2s)^2$ Be are comparable with regard to the quantum numbers of the states involved; in Be, however, there are twice as many exchange terms. That the exchange effects in these two states differ by roughly a factor of 2 in absolute magnitude is thus not surprising. The percent of error in $H_z\Phi$ due to the neglect of exchange is, however, very different from that in Be, where there is not only an error due to neglect of the polarizing effect of the outer electron on the core, which has its analog in the excited He, but also a very large error due to failure to treat the interactions of the $2s$ electrons in a detailed manner. In such a case as this the Fock method does not offer a significant improvement over the Hartree method.

Abandonment of the orbital idea, the difference between $F\Phi$ and $R\Phi$, permits a partial adjustment of the relative positions of the electrons. In both of the states of He a third of the error of the Fock function is thus removed. This may be taken as a rough measure of the general effectiveness of this modification. Thus, for instance, a function similar to $R\Phi$ applied to the treatment of Be might give an error in the first two ionization energies as small as 1.0 ev. Further reduction of this error, associated principally with the treatment of the $2s$ electrons, would require the very difficult step of introducing explicitly the distance between the $2s$ electrons.

Table II. *Errors in computed energy necessary for removal of two electrons.*

	$(1s)^2\ ^1S$ He	$1s2s\ ^1S$ He	$(1s)^2(2s)^2$ Be
$H_z\Phi$	1.14[10]	0.185	1.95[13]
$F\Phi$		0.078	1.61[13]
$R\Phi$	0.70[1]	0.052	

Radial Charge Densities

It is something of a problem to find a satisfactory method for portraying the wave functions of the different types, with the special object of facilitating intercomparisons. Fig. 1 shows the total radial charge densities; in order to avoid confusion due to overlapping, we have plotted a single curve for our best function, and indicated by an enlarged difference plot how the other values deviate from this. $C\Phi$ gives a charge density of the form $\rho_r = r^2\sum_{\sigma,\tau} C_{\sigma\tau} e^{-\delta_\sigma r} r^\tau$. The coefficients are shown in Table III. Though useful for certain purposes, the total density is not adequate for a careful study of the functions, since it suppresses the most interesting characteristics of the better functions, which take into account in detail the interaction of the electrons. Thus, although the total density given by $R\Phi$ is much better than any of the others without r_{12}, it would be a mistake to conclude that $R\Phi$ is itself a correspondingly close approximation to the correct function, as consideration of the errors in the energy will show. On the other hand, in cases where only the charge density is of interest it may be a helpful simplification to use functions of this type. Improvement of the dependence of the functions on interelectronic distance will be seen to result in an increase in the charge density for the smaller values of r, when the electronic repulsions are most important. This is probably a general behavior.

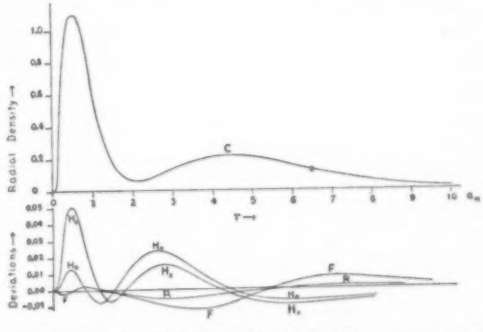

Fig. 1. Total radial charge densities. Upper figure shows values for $C\Phi$. Lower figure shows values for other functions minus those for $C\Phi$. Normalized to 2 on integration over r.

TABLE III. *Constants in formula for total charge density of* $C\Phi$ $\rho_r = r^2 \Sigma_{\sigma,\tau} e^{-\delta_\sigma r} C_{\sigma\tau} r^\tau$.

σ	δ_σ	$C_{\sigma,-2}$	$C_{\sigma 0}$	$C_{\sigma 1}$	$C_{\sigma 2}$	$C_{\sigma 3}$	$C_{\sigma 4}$
1	1.155	−0.02237	0.07185	−0.10055	0.10313	0.00738	0.00013
2	1.6275	.01346	−.01260	−.19053	−.14547	−.00476	
3	2.1	.03986	.23617	.16818	.04403		
4	2.6775	.18754	−.12678	−.16386	−.10751	.05943	.00199
5	3.15	−.19766	.70711	.19377	−.01275	−.03667	
6	4.2	−.06098	37.37703	2.90319	1.26657	.02744	.02464
7	5.355	−12.83385	−8.66312	−2.91047	−.57610	.01630	
8	5.8275	14.76190	6.80816	1.54834	.72437		
9	6.3	−1.88790	1.48937	1.68280			

On the other hand it cannot be expected in general that, as is observed here, the true radial density will be between those given by $H\Phi$ and $F\Phi$, for as we shall see, the relation between these functions varies with the system treated.

COMPARISON OF HARTREE AND FOCK FUNCTIONS

The product functions $H\Phi$ and $F\Phi$ can be compared by plotting or tabulating their separate $1s$ and $2s$ factors. Table IV gives the results for $F\Phi$, the quantities tabulated being the "radial amplitudes" $c_1 rK(r)$ and $c_2 rL(r)$, with c_1 and c_2 so chosen that each factor separately will be normalized with respect to integration over r alone. Since these two factors are not orthogonal, these normalization constants are not the proper ones for constructing a normalized atomic function; for the same reason, caution should be observed in comparing these orbitals with those given by other authors who have used the Fock method in problems where the symmetry was such as to permit solution in terms of orthogonal orbitals. In such cases comparison should be based on the complete atomic functions. Fig. 2 shows our $2s$ factors of $H\Phi$ and $F\Phi$; the $1s$ factors would on this scale be imperceptibly different from the He^+ orbital, and are not shown. The figure shows that the $2s$ factor of $F\Phi$ is more diffuse than that of $H\Phi$; this difference of course carries over into the total charge density, since that due to the $1s$ factor and to the exchange is nearly the same in both cases. Fig. 1 shows that the total charge density due to $F\Phi$ is somewhat excessive at large r, while both $H_0\Phi$ and $H_x\Phi$ err more seriously in the opposite direction. These results contrast with those of Hartree and Hartree,[13] who find for Be that the Fock density is more compact than that given by the self-consistent field theory, and surmise that this is a general relation. The origin of the difference is not far to seek. In the case of excited He, the exchange term occurs with a positive sign, just as in the Heitler-London treatment of two attracting H atoms; and for the same reason: there exists a degeneracy of configurations of the same total spin. In Be, and in general in atoms where the inner shells are filled, the situation resembles that of two repelling He atoms, in which there is no degeneracy of configurations and the exchange terms have negative coefficients. It is not surprising that the effects of considering exchange should be of opposite character in these contrasting cases. Similar remarks apply to the mean values of r^2 corresponding to $F\Phi$ and $H_x\Phi$. We find the former some 16 percent greater (see Table I), while in Be it is 11 percent smaller. (The Hartrees give 8.42 and 9.54 as the respective contributions from each electron in the $2s$ orbit. A rough numerical integration of their $1s$ function gives 0.23 as the corresponding $\bar{r}^2$, making the mean values per electron 4.32 for $F\Phi$ and 4.88 for $H_x\Phi$.) This result, however, is to be expected only in excited atoms, and therefore is hardly an objection to the general usefulness of the statement made by the Hartrees, that wave functions calculated by the method of the self-

TABLE IV. *Radial functions in* $F\Phi$.

r	$c_1 rK(r)$	$c_2 rL(r)$	r	$c_1 rK(r)$	$c_2 rL(r)$	r	$c_2 rL(r)$
0.2	0.756	0 1033	2.4	0.114	−0.2487	6.4	−0.3787
0.4	1.014	0.1513	2.6	0.083	−0.2890	7.2	−0.3205
0.6	1.021	0.1601	2.8	0.061	−0.3261	8.0	−0.2615
0.8	0.913	0.1422	3.0	0.043	−0.3582	9.0	−0.1949
1.0	0.766	0.1066	3.4	0.022	−0.4071	10.0	−0.1406
1.2	0.617	0.0608	3.8	0.011	−0.4406	11.0	−0.0987
1.4	0.484	0.0086	4.2	0.005	−0.4573	12.0	−0.0671
1.6	0.372	−0.0459	4.6	0.003	−0.4602	13.0	−0.0456
1.8	0.281	−0.1006	5.0		−0.4533	14.0	−0.0302
2.0	0.210	−0.1528	5.4		−0.4388	15.0	−0.0197
2.2	0.155	−0.2026	5.8		−0.4181		

[13] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A150**, 9 (1935).

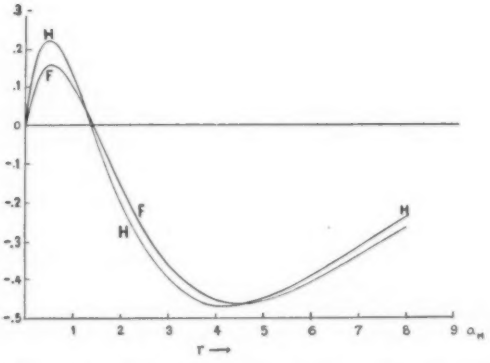

FIG. 2. 2*s* orbitals of Hartree function (*H*) and Fock function (*F*). Curves show $rL(r)$, normalized to 1 on integration over r.

consistent field appear always to give too large a value for the diamagnetic susceptibility.

THE POLARIZATION METHOD

The relation between the Fock function and those which are not restricted to the orbital form may be qualitatively understood with the aid of the polarization theory developed by Hylleraas[14] and Bethe.[7] The method, primarily applicable to highly excited atoms, makes use of a separation of variables similar to that generally used in molecular problems. The outer electron is regarded as moving so slowly in comparison with the inner that the motion of the latter is essentially that of a particle about two fixed centers, and may be represented by a wave function $u_2(1)$, a solution of the differential equation

$$(-\tfrac{1}{2}\nabla_1^2 - Z/r_1 - Z/r_2 + 1/r_{12})u_2(1) = E_2 u_2(1),$$

which is regarded as a function of the coordinates of electron 1 only, those of electron 2 entering as parameters. This function will differ from $K(1)$, the Hartree inner orbital, by being shifted in a direction away from the instantaneous position of the outer electron, so that its repulsive effect upon the latter is reduced. The outer electron is in turn considered as moving in the field of the thus polarized inner distribution plus that of the nucleus; its motion will be described by $v(2)$, a solution of a non-Coulomb central field problem. Clearly $v(2)$ will be more compact than the corresponding Hartree orbital, in determining which the polarization of the inner orbital was neglected. As an approximate solution of the wave equation one then takes the definite function $\psi = u_2(1)v(2)$; there are no further steps of successive approximation, so long as polarization is dealt with in this manner.

In the case of a moderately excited atom the reasoning loses sharpness. In the first place, there is a considerable probability of the electrons being at comparable distances, so that neither can be regarded as almost stationary. In such configurations, we must (in terms of the classical analogy) think of the orbit of each electron as somewhat polarized by the instantaneous proximity of the other, but to only a fraction of the extent which would be caused by a stationary electron, since the actual electron does not occupy any given position long enough for the full effect to develop. The polarization correction as given by the Hylleraas-Bethe theory will therefore be excessive in the region of penetration. In the second place, the exchange terms required by symmetry are not negligible, and their interpretation is not clear. It is assumed that $\psi = u_2(1)v'(2) + u_1(2)v'(1)$, in which $u_2(1)$ is the function obtained above, while $v'(2)$ is the solution of the variational problem in which the energy of the complete function is minimized. To a first approximation the corrections due to exchange will be independent of the polarization corrections, and one may expect $v(2)$ and $v'(2)$ to be related in the same way as the outer orbitals given by the Hartree and Fock methods, respectively.

We shall now show that even in the comparatively little excited state which we are now considering, the qualitative, and to some extent the quantitative, properties of our functions are those indicated by this theory.

An exact calculation of $u_2(1)$ would be very difficult. Bethe[7] and Ludwig[15] have applied a perturbation method, starting with the simple He^+ function $u^0(1)$, and calculating the first-order perturbation produced as the outer electron moves in from infinity. They use an expansion in surface harmonics, and obtain only the terms in P_1 and P_2, the first being much the more important. We have obtained a general formula for

[14] E. A. Hylleraas, Zeits. f. Physik **66**, 453 (1930).

[15] G. Ludwig, Helv. Phys. Acta **7**, 273 (1934).

these terms, and have included in our computations terms in P_0 and P_3. (Details are reserved for a separate section.) The new terms are small except when the second electron is only slightly beyond the first, or even inside it,—that is, for configurations for which the basic ideas of the method break down anyway.

The function $v(2)$ has received practically no discussion by previous authors, who have been concerned primarily with determining energy values, for which purpose they have used Fock or even hydrogenic outer orbitals, as being sufficiently good in the case of highly excited states. We have not attempted to determine $v(2)$ directly, but have investigated an "empirical" $v(2)$ of form so chosen that, when combined with our approximate values of $u_2(1)$, it reproduced $C\Phi$ as well as possible. In the outer regions, this function is well defined by the total radial density; since the exchange terms are negligible here and $u_2(1)$ is normalized for integration over $d\tau_1$, the density gives immediately the square of $v(2)$. In the inner region, the choice of $v(2)$ becomes increasingly arbitrary; no values can be found which give consistent agreement, and those selected will serve as well as any to show the magnitude and nature of the discrepancies.

In Table V are indicated values of the assumed $v(2)$, the corresponding atomic function $P\Phi$, and $C\Phi$, for several configurations. We also include the angle variations (differences in the function for configurations with the same r_1 and r_2, but minimum and maximum values of r_{12}, compared with the mean value over all values of r_{12}). This table shows that, as expected, the function $v(2)$, in the region where it is well defined, is appreciably more compact than the Fock outer orbital, and that it leads to an atomic function in quite satisfactory agreement with the correct function, both in absolute magnitude and in angle variation. The angle variation furnishes a particularly good test of the polarization theory, since the values calculated are only slightly dependent upon the form assumed for $v(2)$. In the inner region, on the other hand, the agreement becomes much worse, and the angle variation according to the polarization computation is much too large, likewise as expected.

Reasoning similar to that above can be applied to the determination of the function $R\Phi$. The inner function $u_2(1)$ now describes the motion of the first electron in the field of a second electron distributed over a sphere with radius r_2; the first-order correction is given by the term in P_0 of the complete polarization theory. The "polarization" takes the form of an increasing diffuseness of $u_2(1)$ as r_2 becomes smaller. It must also result in some contraction of the outer function $v(2)$, compared with $L(2)$, but the smallness the P_0 term in the polarization correction indicates that this should be insignificant, except for very small r_2.

Comparison of the Fock Function with More Accurate Forms

Except for the complication introduced by the exchange terms, we have now a basis for comparison between $R\Phi$ and $F\Phi$. In Fig. 3, we have plotted $r_1r_2R\Phi$ in the form of a series of curves for fixed values of r_1, which we may regard as cross sections of the surface representing $r_1r_2R\Phi$ as a function of r_1 and r_2. These cross sections are practically indistinguishable on this scale from those corresponding to $F\Phi$. For small r_1, they have essentially the character of a $2s$ orbital, while, as r_1 increases, they pass over into the $1s$ orbital form. The exchange effect, a necessary consequence of the symmetry of the function, largely masks that due to polarization. It happens, however, that, for $r_1=0.2$, $F\Phi$ gives $r_1K(1)=0.756$, $r_1L(1)=0.1033$, while for $r_1=1.0$ we find $r_1K(1)=0.766$, $r_1L(1)=0.1066$. A comparison of the corresponding cross sections for $R\Phi$ and $F\Phi$ therefore practically eliminates the exchange effect, since the amounts of $1s$ and $2s$ orbitals present in $F\Phi$ are almost the same in both cases, and the exchange effect is supposed independent of the polarization correction. These cross sections are shown in Fig. 4. For large r_2 and small r_1, both $F\Phi$ and $R\Phi$ reduce practically to the single terms $K(1)L(2)$ and $u_2(1)v(2)$. Further, $u_2(1)$ is, as shown by computation, practically indistinguishable from $K(1)$, so that in this region we are essentially comparing $v(2)$ with $L(2)$; it is seen that the difference between $R\Phi$ and $F\Phi$ is practically the same for both values of r_1 and corresponds to a slight contraction in the outer function. On the other hand, when both r's are small the two terms in the function

TABLE V. *For comparison of functions (normalized to $(4\pi)^2$) at various points.*

		$r_1=0.4$		$r_1=0.8$		$r_1=1.6$		$r_1=3.0$		$r_1=6.4$	
	0.2979	0.2621	−0.1260	0.2790	0.2513	−0.0719	0.0215	0.0077	−0.0051	−0.3607	−0.3608	−0.0021	−0.3772	−0.3754	+0.0014
		.3001	− .0602		.2812	− .0113		.0153	+ .0028		− .3675	+ .0006		− .3763	+ .0010
$r_2=0.4$	.3058	.3191	− .0198	.2814	.3026	+ .0280	.0095	.0217	+ .0090	− .3555	− .3737	+ .0030	− .3828	− .3770	+ .0005
		−.1038	− .0380		−.0905	− .0299		−.0155	− .0076		.0040	.0067		.0013	.0009
		.0594	.0190		.0607	.0213		.0126	.0064		− .0037	− .0062		− .0012	− .0006
				.2507	.1920	− .0732	.0105	−.0060	− .0157	− .3226	− .3167	− .0044	− .3368	− .3349	+ .0008
					.2492	+ .0008		.0028	.0009		− .3329	− .0006		− .3374	+ .0001
			$r_2=0.8$	.2589	.2779	+ .0394	.0107	.0091	+ .0079	− .3200	− .3465	+ .0032	− .3448	− .3397	− .0004
					−.1312	− .0572		−.0245	− .0088		.0124	.0162		.0032	.0025
					.0672	.0286		.0142	.0063		− .0097	− .0135		− .0028	− .0023
								−.0369	.0174	− .1393	− .1219	+ .0050	− .1371	− .1323	+ .0001
							−.0446								
								−.0493	− .0007		− .1430	+ .0005		− .1359	− .0002
							−.0340			− .1345			− .1401		
						$r_2=1.6$		−.0558	− .0081		− .1577	+ .0010		− .1390	− .0003
								.0307	.0126		.0307	.0211		.0040	.0036
								−.0137	− .0063		− .0142	− .0147		− .0031	− .0031
											− .0208	.0090		− .0141	.0001
										− .0320			− .0156		
											− .0334	.0015		− .0154	− .0001
									$r_2=3.0$	− .0311			− .0164		
											− .0397	− .0004		− .0164	− .0001
											.0201	.0126		.0016	.0013
											− .0082	− .0063		− .0010	− .0010
														− .0448	.000019
														− .0471	− .000002
												$r_2=6.4$		− .0482	− .000009
														.0044	.000023
														− .0018	− .000011

Key

Entries are r_1r_2 times values of functions, or differences, arranged thus:

$R\Phi$	$C\Phi_{\min}$	$P\Phi_{\min}-C\Phi_{\min}$
$F\Phi$	$\overline{C\Phi}$	$\overline{P\Phi}-\overline{C\Phi}$
	$C\Phi_{\max}$	$P\Phi_{\max}-C\Phi_{\max}$
	Angle variation in $C\Phi$	Angle variation in $P\Phi$

Comparison of assumed $v(r)$ with $L(r)$

r	0.4	0.8	1.6	3.0	4.2	5.4	6.4	7.2	8.0
$rv(r)$	0.1500	0.1400	−0.0670	−0.3770	−0.4677	−0.4371	−0.3692	−0.3072	−0.2476
$rL(r)$	0.1513	0.1422	−0.0459	−0.3582	−0.4573	−0.4388	−0.3787	−0.3205	−0.2615

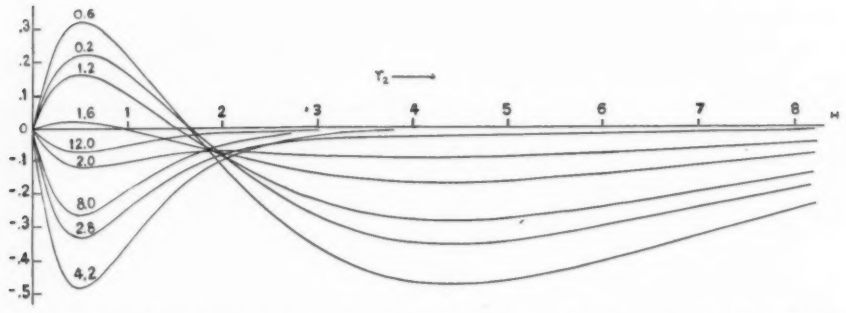

FIG. 3. Values of best function of r_1 and r_2. Curves give $r_1 r_2 R\Phi$ as functions of r_2 for the indicated values of r_1. On the scale shown, $R\Phi$ is normalized to $16\pi^2$ on integration over coordinate space.

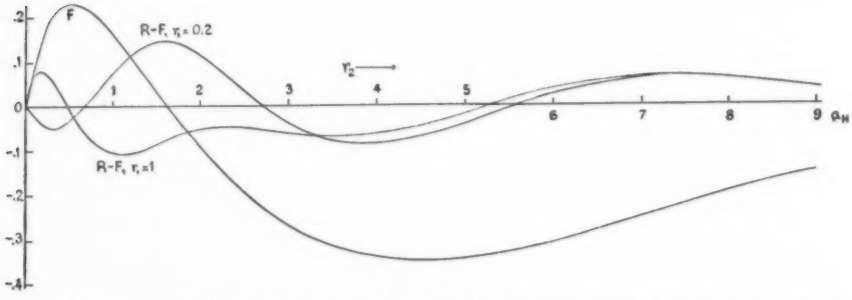

Fig. 4. Comparison of $R\Phi$ and $F\Phi$. Curve F shows values of $r_2 F\Phi$, for $r_1=0.2$ and for $r_1=1.0$, the values being too close together for separate representation. The other curves show, ten times enlarged, the values of $r_2(R\Phi-F\Phi)$ for r_1 as indicated. Normalization as in Fig. 3.

are of comparable importance, and both must be somewhat affected by polarization. We might represent $R\Phi$ as $K(1)L(2)g(1,2)+L(1)K(2)h(1,2)$, where the factors $g(1,2)$ and $h(1,2)=g(2,1)$ have, both separately and in combination, the character of moving the average distribution of electron 2 in or out, respectively, accordingly as the known position of electron 1 moves out or in. In the Fock function $L(2)$ and $K(2)$ are distributions in the field of the average distribution of electron 1. In $R\Phi$, however, $L(2)g(1,2)$, as a function of 2, is more diffuse than this if the fixed electron (considered as a K electron) is at an unusually small $r(0.2)$ and less diffuse if it is at a greater than average $r(1.0)$. On the other hand, $K(2)h(1,2)$ is in both cases more diffuse than the Fock orbital $K(2)$, since 0.2 and 1.0 are both much smaller than the average distance of an L electron. The term $K(1)L(2)g(1,2)$ is the principal part of the function for intermediate values of r_2, and it may therefore be expected that the Fock cross section should lie between the other two in this region. For still smaller distances the polarization idea breaks down completely and the theory ceases to be helpful; it remains true, however, that the Fock cross section lies between the other two.

$C\Phi$ differs from $F\Phi$, to an even greater extent than does $R\Phi$, in assigning a larger probability to the appearance of the two electrons at approximately the same r. This is, of course, not correlated with a corresponding increase in the indicated chance of the two electrons approaching each other, for the favored configurations place the electrons on opposite sides of the nucleus. At large r the charge density is distinctly more compact than for $F\Phi$ and $R\Phi$, as indicated by the polarization theory. In our diagram their difference in form between $R\Phi$ and $C\Phi$, really more pronounced than that between $F\Phi$ and $R\Phi$, is somewhat disguised by the different normalization of the outer parts of the distributions.

Table V will illustrate the importance of the dependence of $C\Phi$ on r_{12}, particularly for the

smaller values of r_1 and r_2. Here the differences in $C\Phi$ with varying r_{12} are much greater than the differences between $R\Phi$ or $F\Phi$, and $\overline{C\Phi}$, the mean value of $C\Phi$ for given r_1 and r_2. $R\Phi$ is in fact a fairly good approximation to $\overline{C\Phi}$ everywhere; from this the satisfactory agreement of the charge densities for $R\Phi$ and $C\Phi$ follows.

Complete Determination of First-Order Polarization of the Core

We require a solution of the equation

$$(\tfrac{1}{2}\nabla_1^2+E(r_2)+Z/r_1+Z/r_2-1/r_{12})u_2(1)=0, \qquad (1)$$

where r_2 is considered as a fixed parameter, and $u_2(1)$ is a function of the coordinates of electron 1 which depends upon the position of electron 2. We regard $(1/r_{12}-1/r_2)$ as a perturbation term, small of the first order. Then, in terms of the new variables

$$\rho=Zr_1, \quad R=Zr_2,$$

we find the zeroth approximations for solution and energy to be

$$u^0(1)=(Z/2)ce^{-\rho}, \quad c^2=4Z/\pi; \quad E^0(R)=-\tfrac{1}{2}Z^2-Z(Z-1)/R.$$

To the first order, the energy is $E^0(R)+\epsilon_1(R)$; where $\epsilon_1(R)=-Ze^{-2R}(1+1/R)$. The first approximation for the solution is assumed to have the form

$$u_2(1)=u^0(1)\{1+\sum_{n=0}^{\infty} f_n(1,2)P_n(\cos\theta_{12})\}. \qquad (2)$$

To determine the $f_n(1,2)$, we expand $1/r_{12}$ in spherical harmonics, substitute (2) in (1), and equate terms of corresponding order of smallness and involving the same harmonics. Let $u^0(1)f_n(1,2)=\varphi_n(\rho)$. There result the equations

$$\varphi_0''-\varphi_0+2(\varphi_0'+\varphi_0)/\rho = ce^{-\rho}\begin{cases}e^{-2R}(1+1/R) \text{ for } \rho<R,\\ [e^{-2R}(1+1/R)+1/\rho-1/R] \text{ for } \rho>R.\end{cases} \qquad (3)$$

$$\varphi_n''-\varphi_n+2(\varphi_n'+\varphi_n)/\rho-n(n+1)/\rho^2 = ce^{-\rho}\begin{cases}\rho^n/R^{n+1}, & \rho<R,\\ R^n/\rho^{n+1}, & \rho>R,\end{cases} \quad n>0. \qquad (4)$$

Ludwig gives the solutions of these equations for $n=1, 2$. (Through an error, he introduces a factor 2 on the right side, but his solutions are correct except that in his Eq. (15a) $(1+R^2)$ should read $(1+R)^2$.) The general solution for $n>0$ may be obtained in the same way.

The case $n=0$ presents some interesting peculiarities. For the region $\rho<R$, a particular solution, everywhere finite, is found to be

$$\varphi_{1a}=\tfrac{1}{2}e^{-2R}(1+1/R)ce^{-\rho}[Ei(2\rho) -\log(2\rho)-\rho-(e^{2\rho}-1)/2\rho]. \qquad (5)$$

To this may be added a constant, $\alpha(R)$, times that solution of the homogeneous equation which remains finite for $\rho\to 0$. Similarly, for $\rho>R$ a particular solution, vanishing properly at infinity, is

$$\varphi_{out}=\tfrac{1}{2}ce^{-\rho}\{[e^{-2R}(1+1/R)+1-1/R] \times[1/2\rho-\log(2\rho)-\rho]+\rho\}. \qquad (6)$$

To this may be added a constant, $\beta(R)$, times that solution of the homogeneous equation which vanishes properly for $\rho\to\infty$. One would expect the constants α and β to be determined by the conditions that the two solutions and their derivatives must have the same values at $\rho=R$. However, it turns out that the two required solutions of the homogeneous equation are identical, namely, $u^0(1)$ itself. Continuity of function requires

$$\beta-\alpha=\beta^0=(1/Z)\{(e^{-2R}Ei(2R)-1)(1+1/R) +\log(2R)(1-1/R)\}, \qquad (7)$$

and it is found that this relation also leads to continuity of derivative.

There are therefore an infinite number of solutions of the complete equation which satisfy the boundary conditions. The one desired is that which is orthogonal to the unperturbed solution (a requirement which does not need to be considered when $n>0$, since orthogonality is assured by the presence of the factor $P_n(\cos\theta_{12})$). We have, therefore, (since $u^0(1)$ is normalized),

$$\alpha(R)=-(4\pi/Z^3)[\int_0^R \varphi_{in}u^0\rho^2d\rho +\int_R^\infty(\varphi_{out}+\beta^0u^0)u^0\rho^2d\rho]. \qquad (8)$$

The final expressions for $f_n(1,2)$ may be conveniently thrown into the form:

For $\rho<R$, $f_n=-(1/Z)\{A_n(\rho)B_n(R) +[C_n(\rho)-D_n(\rho)]E_n(R)+H_n(R)\}$.

For $\rho>R$, $f_n=-(1/Z)\{C_n(\rho)[E_n(R) -F_n(R)]-G_n(\rho)R^n+K_n(R)\}$.

For $n=0$, we find

$A_0(x)=1$ $\qquad B_0(x)=0$

$C_0(x)=1/2x-x-\log(2x)$ $\qquad D_0(x)=e^{2x}/2x-Ei(2x)$

$E_0(x)=-e^{-2x}(x+1)/x$ $\qquad F_0(x)=(x-1)/x$

$G_0(x)=x$

$H_0(x)=e^{-2x}\{x+2C-\frac{3}{2}+(2C-1)/x +(1+1/x)\log(2x)+(1-1/x)e^{2x}Ei(-2x)\}$.

$K_0(x)=H_0(x)-\{(e^{-2x}Ei(2x)-1)(1+1/x) +\log(2x)(1-1/x)\}$.

C represents Euler's constant.

For $n>0$, we let $n(n+1)/2=m$; then

$A_n(x)=(n+1)x^n+nx^{n+1}$. $\qquad B_n(x)=1/2mx^{n+1}$.

$C_n(x)=1/m+1/x+m/2!x^2+m(m-1)/3!x^3 +m(m-1)(m-3)/4!x^4 +m(m-1)(m-3)(m-6)/5!x^5+\cdots$.

$D_n(x)=\tfrac{1}{2}e^{2x}(-1)^{n+1}\{1/x^2-(m-1)/x^3 +(m-1)(m-3)/2!x^4-\cdots\}$.

$E_n(x)=\tfrac{1}{2}e^{-2x}(-1)^{n+1}(2n+1)(1+x)\{1/x +m/x^2+m(m-1)/2!x^3+\cdots\}$.

$F_n(x)=-\tfrac{1}{2}(2n+1)(1+x)\{1/x-m/x^2 +m(m-1)/2!x^3-\cdots\}$.

$G_n(x)=(n+(n+1)x)B_n(x)$.

$H_n(x)=0$. $\qquad K_n(x)=0$.

On the Ground State of Lithium*

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Wave functions of several forms have been applied to the treatment to the ground state of Li. It is found that errors in the representation of the K shell have but little effect on the computed ionization energy, and that a satisfactory orbital for the L electron can be constructed in a very simple form. The best wave function in which the relative positions of the K and L electrons are not taken into account gives an ionization energy in error by 0.05 ev. To take account of inter-shell polarization effects the Hylleraas method has been extended, and a wave function has been constructed which depends on the relative positions of all the electrons. A total energy in error by 0.068 ev (0.034 percent) has been computed, and the theoretical value of the ionization energy is fixed as 5.363 ± 0.007 ev against an observed 5.364 ev.

INTRODUCTION

THE lithium atom, a simple system with all the essential characteristics of the other more complicated and perhaps more interesting alkali metal atoms, has been the subject of several wave-mechanical investigations.[1] All these treatments have been characterized by the construction of the atomic wave function from one-electron orbitals, and may accordingly be considered as more or less satisfactory approximations to the Fock procedure.[2] In each case the computed atomic and ionic energies are in error by some 2.0 ev, while the errors in ionization energy (obtained as the difference of the computed atomic and ionic energies) are of the order of 0.1 ev. Wilson has reduced this error to 0.044 ev using for the K electrons the orbital $e^{-2.69r}$, and for the L electron $1.345re^{-0.665r}-e^{-1.5r}$. That so simple a method of treatment should yield such satisfactory values of the ionization energy is a matter of considerable interest. The reliability of these values must suffer, however, from their having been obtained as the difference of two quantities, each of which was much less accurately known; there is also no variation principle to assure us that the true value of the ionization energy is an upper limit monotonically approached by the calculated values as the wave functions improve.

We have therefore been interested in examining the effect on the ionization energy of various approximations in the atom and ion wave functions, in determining the theoretical ionization energy with considerable exactness, and in improving the determination of the energy and wave function of the complete three-electron system. Various steps in the passage from the Wilson function to the most flexible possible form readily suggest themselves. We have examined the following, which appear to be the most important: (a) improvement of the separate orbitals, for which Wilson used functions of somewhat limited flexibility, (b) improvement of the representation of the K electrons by removal of the requirement that they be represented by orbital functions, and (c) complete abandonment of orbitals in the construction of the wave functions of the systems. In the last two stages of our work we have employed the method of Hylleraas, which has been eminently successful in the treatment of the normal and first excited states of He,[3, 4, 5] which have many features in common with the ground state of Li. In principle the extension to the more complicated system is quite simple, but the practical difficulties encountered are rather serious. A description of the way in which these were overcome is reserved for later sections of this paper; we proceed now to a presentation and discussion of the results which we have obtained.

* A preliminary notice of a portion of these results appeared in Phys. Rev. **47**, 700 (1935).

[1] E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933) and references given there.

[2] V. Fock, Zeits. f. Physik **61**, 126 (1930).

[3] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

[4] E. A. Hylleraas and B. Undheim, Zeits. f. Physik **65**, 759 (1930).

[5] A. S. Coolidge and H. M. James (see paper in this issue, p. 676).

Improvement of the Orbital Functions

The wave functions hitherto used in treating Li have been of the form

$$\psi=\begin{vmatrix} K(1)\delta(\alpha/\sigma_1) & K'(1)\delta(\beta/\sigma_1) & L(1)\delta(\alpha/\sigma_1) \\ K(2)\delta(\alpha/\sigma_2) & K'(2)\delta(\beta/\sigma_2) & L(2)\delta(\alpha/\sigma_2) \\ K(3)\delta(\alpha/\sigma_3) & K'(3)\delta(\beta/\sigma_3) & L(3)\delta(\alpha/\sigma_3) \end{vmatrix},$$

where K, K' and L are the space parts of K and L orbitals, while $\delta(\alpha/\sigma_1)$, etc., are the spin functions introduced by Slater.[6] Actually $K(1)$ has always been taken to be identical with $K'(1)$, as would be the case in the ion, but is not required in the atom. Expanding the determinant above, we find $\psi=K'(1)\{K(2)L(3)-K(3)L(2)\}\delta(\beta/\sigma_1)\delta(\alpha/\sigma_2)\times\delta(\alpha/\sigma_3)+$two similar terms which differ by permutations which assign different spins to the electrons. Because of the different spin factors, no combination of two different terms can make any contribution to the matrix element of energy or unity corresponding to this function (so long as the Hamiltonian is assumed independent of the spin), so that these elements will be simply three times the contribution arising from any single term in combination with itself. Now this property can easily be seen to be a general one, possessed by any function having the symmetry appropriate to Li. We may write such a function

$$\psi=\varphi(1,\,2,\,3)\delta(\beta/\sigma_1)\delta(\alpha/\sigma_2)\delta(\alpha/\sigma_3)+\varphi(2,\,3,\,1)\delta(\beta/\sigma_2)\delta(\alpha/\sigma_3)\delta(\alpha/\sigma_1)+\varphi(3,\,1,\,2)\delta(\beta/\sigma_3)\delta(\alpha/\sigma_1)\delta(\alpha/\sigma_2),$$

the only restriction upon $\varphi(1,\,2,\,3)$ being that it must be antisymmetrical in the coordinates of electrons 2 and 3. With this understanding, the whole discussion can be carried out on the basis of the function $\varphi(1,\,2,\,3)$.

For separate-orbital functions, we have

$$\varphi(1,\,2,\,3)=K'(1)\{K(2)L(3)-K(3)L(2)\}.$$

The Fock function is the best function of this form, and it is clear that Wilson's function is not a very close approximation to it. His K orbital in particular was rather inflexible, and a treatment of He using such orbitals gives decidedly poorer results than the Hartree method, and, *a fortiori*, the Fock method. In the next section we shall deal with even more radical changes of the core function than improvement of the orbitals involved, and it will become apparent that no appreciable change in the ionization energy is to be expected from such a modification of Wilson's function. We have therefore been interested only in the effect of increasing the flexibility of the L orbital, changes in which will be more strongly reflected in ionization energy. We find that with an L orbital of the form $L(1)=c_1r_1e^{-0.665r_1}+c_2e^{-1.25r_1}+c_3e^{-1.5r_1}+c_4e^{-1.75r_1}$ improvement of just 0.002 ev over Wilson's value could be obtained. An attempt to make a similar improvement in his function by replacing the term $r_1e^{-0.665r_1}$ by $c_1r_1e^{-\alpha_1r_1}+c_2r_1e^{-\alpha_2r_1}+c_3r_1e^{-\alpha_3r_1}$ gave no gain at all. Evidently Wilson's L orbital, though of very simple form, is about as good as any which might be used in functions of this type; of the residual error in his ionization energy only 0.002 ev can be attributed to lack of flexibility in this orbital.

Improvement in Inner Shell Representation

In the description of Li, the use of orbitals in connection with the K electrons is clearly inadequate, as it is in the treatment of the analogous He. The representation may be improved by similar methods, thus giving us a function of the separate-shell type, for which the general form is

$$\varphi(1,\,2,\,3)=KK(1,\,2)L(3)-KK(1,\,3)L(2),$$

where $KK(1,\,2)$ is an unrestricted function of the relative coordinates of the two electrons, having the general nature of a wave function for Li^+, but not necessarily symmetrical in 1 and 2.

We have computed the energy of a number of functions of this form, both with the simple outer function $L=re^{-0.65r}$, and with the better one $L=1.4re^{-0.65r}-e^{-1.5r}$, which is nearly the same as Wilson's. Table I contains the results, as well as a description of the core functions investigated. With the exception of E, the core functions will be recognized as of the Hylleraas type, modified as discussed in our paper on excited He.

Function E is of a new type, which can be regarded as derived from a Hylleraas function by expanding the powers of r_{12} as functions of r_1, r_2, and $\cos\theta_{12}$, and then selecting a finite number of the resulting terms, with coefficients to be varied independently. In these terms there are dis-

[6] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

TABLE I. *Variation of ionization energy with inner shell functions.*

Energies in electron volts.

Inner Function Alone			Combined with P		Combined with Q	
Symbol	Ion energy	Error	Atom	Error in ionization	Atom	Error in ionization
A	−192.89	+4.22	−198.19	−0.060	−198.27	+0.019
B	−195.49	+1.62	−200.78	−0.077	−200.83	−0.028
C	−195.53	+1.57	−200.82	−0.080	−200.85	−0.048
D	−196.30	+0.81	−201.56	−0.095	.....	.....
E	−197.02	+0.09	−202.28	−0.094	−202.32	−0.057
F	−197.05	+0.05	−202.32	−0.093	.....	.....
Ideal	−197.10	0.00	(−202.37)	(−0.093)	(−202.39)	(−0.056)

The functions used are as follows (not normalized):

A $e^{-3(r_1+r_2)}$.

B $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)]$.

C $e^{-2.6875(r_1+r_2)}$.

D $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)+c_3r_1r_2+c_4(r_1^2+r_2^2)]$.

E $e^{-3(s_{12}+g_{12})}[c_1+c_2g_{12}+c_3s_{12}^2g_{12}^{-1}+c_4g_{12}^2+c_5s_{12}+c_6s_{12}\cos\theta_{12}+c_7s_{12}^{-1}\cos^2\theta_{12}]$.

F $e^{-3(r_1+r_2)}[c_1+c_2(r_1+r_2)+c_3r_1r_2+c_4(r_1^2+r_2^2)+c_5r_{12}+c_6r_{12}^2]$.

P $r_{12}e^{-0.55r_{12}}$.

Q $1.4r_{12}e^{-0.55r_{12}}-e^{-1.5r_{12}}$.

The coefficients c_n were determined so as to minimize the ion energy. In constructing the atomic function, the same values were used.

The symbols g_{12} and s_{12} in function E represent, respectively, the greater and the smaller of r_1 and r_2.

The last row is an extrapolation, in which the error in the ion energy has been made to vanish.

continuities of derivative when $r_1=r_2$ which make finite contributions to the kinetic energy, but do not destroy their usefulness. We have applied such a function to the treatment of the ground state of He, and with the inclusion of nine terms have reduced the error in the computed energy to less than 0.02 ev. Since this error is some three times that given by Hylleraas' six-term function and the computations are no easier these functions are not recommended as a substitute under such conditions. It was found, however, that when it was desired to add a third electron to the system and to neglect polarization terms with this electron (as in the present case) the treatment was more conveniently carried out with this than with the Hylleraas function; hence the present computation. This ceases to be true, however, when inter-shell polarization effects must be included. Since functions of this type seem to be restricted in usefulness and the methods of handling them in the three-electron problem are quite complicated we omit any further description of them.

It is apparent from Table I that, for the given L orbitals, the ionization energy comes out almost independent of the representation of the inner shell, so long as the latter is not too bad, and that the small changes which do occur are similar with both orbitals. This would undoubtedly hold for any good L orbital. An obvious corollary is that when L has been given the best form for use in conjunction with some reasonably good core function, this will be very nearly the best form for any other good representation of the inner shell. As an example, we note that the linear coefficient in function Q is essentially the same whether it minimizes the atomic energy with core C or with core E. Now, computation with core function C has shown that Wilson's L function gives a result better than function Q by 0.004 ev, and that a further 0.002 ev can be gained by still further improving the outer orbital. In view of the above discussion we may confidently expect that the values in the last column of Table I (at least the last few entries, in which we are primarily interested) would be likewise raised by 0.006 ev if Q were replaced by the best possible L function.

The core functions from A to F are progressively better approximations to the true ion function. It is of interest to attempt an extrapolation to determine the energy which would be obtained by combining this function with various outer orbitals. The last row of Table I gives such estimates. In particular, if the best possible L function were used, the residual error would be very close to −0.050 ev, which is evidently the error inherent in the forced separation of the shells.

In the examples so far given the core function and the ion function have been identical, and there seems to be no doubt as to the propriety of computing the ionization energy as the difference of the computed energies of atom and ion. The best function for the atom core having a given form will, however, presumably differ from the best ion function of the same form; in fact, as has already been pointed out, the ion function has different symmetry properties from the best core function. Thus there arises the question as to how the ionization energy shall be determined. In order to investigate this point, we made computations differing from the $F-P$ combination of Table I in that, in the first case, the coefficients c_n were allowed to take on values minimizing the atomic energy, and, in the second case, in that this adjustment was made after separate coefficients were assigned to the terms in r_1 and r_2, and to those in r_1^2 and r_2^2. In the first case the energy was reduced by 0.0003 ev, while the second charge permitted a further improvement of 0.0002 ev. We conclude that there is no

significant difference between the best ion function and the best core function obtainable with a given series of the sort which we use. This is fortunate, for it relieves us of the necessity of determining the coefficients of the ionic function and introducing them explicitly as restrictions upon the variation carried out to give the corresponding atomic function. We need only solve the secular equations for atomic and ionic problems, and take the difference as the ionization energy. It also enables us to save labor by assuming that terms which in the ionic function must have the same coefficient may be treated as preserving this relation in the atom, thereby forming, for purposes of variation, a single term.

Physical Interpretation

Qualitatively, these results are easy to understand. If we had complete flexibility in both KK and L, we should arrive, on minimizing the total energy, at a definite function of a rather interesting type, in which the relation between the L electron and the K shell taken as a whole is formally that between the L and K electrons in excited He, particularly in the $1s2s\ ^3S$ state, according to the Fock approximation. In line with our discussion of the Fock function for the corresponding singlet state (no treatment of the triplet state being available), we may expect the defects of this function to be, speaking roughly, that it neglects the polarization of the core by the valence electron and the consequent contraction of the outer orbit, thereby yielding too high a total energy. We would also expect that the K shell function will be but slightly different from that of the free ion. Both the distortion of the ion function and the polarization effects should be less pronounced in Li than in $1s2s\ ^3S$ He, because the core electrons are more firmly bound. Now, in $1s2s\ ^1S$ He, we have found that the defects of the Fock function are responsible for an energy error of 0.078 ev; this should be less for the triplet state because the electrons are to some extent kept apart by the antisymmetry. The error in the total energy of the best separated-shell function (indicated by SS) for Li should then be a few hundredths of a volt only, and this will also be the error in the ionization energy if we disregard the difference between the correct ion function and the KK factor in our atomic function.

As computed for a separated-shell function the energy is roughly separable into energy of the core, energy of the valence electron in the average field of the core, and exchange energy, of which the last two parts give the ionization energy. Starting with the function SS, we may replace the core factor by another which may contain large errors with respect to the mutual relations of the core electrons, but which has substantially the same average field. While the total energy will be seriously affected, the ionization energy will be influenced only through the variation of the exchange term, a second-order effect which might be of either sign. On the other hand, if the L orbital is varied the change in the ionization energy will arise principally from modification of the energy of the valence electron, with the change in exchange energy making a second-order contribution. Thus the ionization energy is essentially a characteristic of the L orbital used, with a minor dependence on the core function through the exchange energy. When functions permitting separation of the shells give ionization energies in error by less than 0.05 ev, as in Wilson's work, this cannot be taken as evidence that the function is a good one; thus, it is clear from Table I that some combination of A and B could be found to give exactly the correct ionization energy. This effect is due to the compensating errors in the exchange energy which arise from a poor core function. To obtain a more accurate value for the ionization energy which is also reliable one must deal with the mutual polarization of the K and L shells. It is to this problem that the next section of this paper is devoted.

Inclusion of Polarization Effects Between the Shells

For the computations of this section, we have extended our modification of the Hylleraas method, constructing new terms in our trial series by multiplication of the terms already found most useful by powers of r_{13} and r_{23} and/or by suitable negative powers of r_3 (assigning the number 3 to the L electron). The new terms (as well as all of those previously discussed except those of the function E) can be specified

as follows: We choose as variables $\rho_1=\kappa r_1$, $\cdots$ $\rho_{23}=\kappa r_{23}$, in which a possible additional degree of flexibility is gained by introducing the scale-constant κ. Let

$$\zeta[k, m, n/\gamma, \delta, \delta] = (\kappa^9/4\pi)^{\frac{1}{2}} e^{-(\gamma\rho_2+\delta\rho_2+\delta\rho_1)} \rho_3{}^k \rho_2{}^m \rho_1{}^n,$$

$$\xi[k, m, n/\gamma, \delta, \delta] = (\kappa^9/4\pi)^{\frac{1}{2}} e^{-(\gamma\rho_2+\delta\rho_2+\delta\rho_1)} \rho_2{}^k \rho_3{}^m \rho_1{}^n.$$

Our terms in the series for $\varphi(1, 2, 3)$ then have the forms

$$f[k, m, n, p] = \rho_{23}{}^p \{\zeta[k, m, n/\gamma, \delta, \delta] - \xi[k, m, n/\gamma, \delta, \delta]\},$$

$$g[k, m, n, p] = \rho_{12}{}^p \zeta[k, m, n/\gamma, \delta, \delta] - \rho_{13}\xi[k, m, n/\gamma, \delta, \delta],$$

$$h[k, m, n, p] = \rho_{13}{}^p \zeta[k, m, n/\gamma, \delta, \delta] - \rho_{12}\xi[k, m, n/\gamma, \delta, \delta],$$

$$f[k^*, m, n, p] = \rho_{23}{}^p \{\zeta[k, m, n/\gamma^*, \delta, \delta] - \xi[k, m, n/\gamma^*, \delta, \delta]\}, \quad \text{etc.}$$

In the bulk of the work of this section, the constants had the values $\delta=3$, $\gamma=0.65$, $\gamma^*=1.5$, $\kappa=1$. We postpone for the present a discussion of their selection, as well as of the choice of appropriate terms. The most general extension of the Hylleraas method would, of course, require provision for terms with powers of two or three interelectronic distances occurring simultaneously, which could not be represented in the above notation. We have avoided this complication. We have also, in accordance with the results of the previous section, treated $\{g[k, m, n, p]+g[k, n, m, p]\}$ as a compound term with a single coefficient. It will be seen that the terms g are just those occurring in the previously discussed functions of the separate-shell type. The new terms f and h allow for detailed treatment of the reactions between the outer electron and the inner one having the same and the opposite spin, respectively.

It might appear that so long as one's interest is restricted to the ionization energy it would be possible to ignore the terms $g[k, m, n, p]$, $p\neq 0$, which permit an accurate treatment of the core. Thus one would regard the atomic function as constructed from a core function, depending on r_1 and r_2, and an L orbital depending on r_3, r_{13}, and r_{23}, and would argue from Table I that the ionization energy should be practically unaffected by change in the core function. But it must be noted that we have no guarantee that results parallel to those in Table I would be obtained if the outer function were freely variable. For r_{12}, r_{13} and r_{23} cannot take on their magnitudes with complete independence, and from this arises the possibility that (in a very awkward manner, to be sure) some defects in the core function might be compensated for by adjustment of the inter-shell polarization terms. Thus with a core function poor enough to bring this effect into play the calculated ionization energy might appreciably exceed the actual value. It is accordingly necessary to carry out the work with core and atomic functions so good that such second-order terms can be safely neglected, and this seems to require a fairly accurate treatment of the effects on each other of the K electrons.

As a basis for our work we have chosen the atomic function constructed from the Hylleraas core function F and the Wilson L orbital, omitting, however, four of the twelve terms with an estimated error of 0.001 ev. To this function we have added nine new terms designed to take account of the polarization effects, obtaining a total energy in error by 0.068 ev. It was possible to make a fairly definite estimate of the limit attainable by the inclusion of indefinitely many such terms, including those with higher powers of r_{13} and r_{23} and combinations of such powers, according to the general method which we have previously explained.[7] Such an estimate indicates a convergence limit in excess of the experimental value by 0.051 ± 0.007 ev. Now, this is, within the limit of uncertainty, exactly the error which we ascribed to the defective core factor of the function before the polarization terms were included,—that is to say, it is the error of the best free ion function which can be constructed out of the terms which remain when we write down the terms in our best atomic function and then strike out all factors referring to r_3, r_{13}, or r_{23}. It appears then that to a satisfactory degree of approximation, the core function retains its identity even in the correct, nonseparable atomic function; that our atomic function is so good an approximation that the errors due to imperfect representation of the inner shell and to incomplete treatment of the polarization are additive. To the extent that this is true, we may speak of the ionization energy corresponding to our func-

[7] H. M. James, A. S. Coolidge and R. D. Present, J. Chem. Phys. **4**, 187 (1936).

tion, even though it is of a nonseparable type. Our best calculated ionization energy is thus 5.347 ev, and the extrapolated value 5.363 ± 0.007 ev, as compared with the experimental 5.364 ev.

We have not determined the coefficients of our best 17-term function. We give here a comparatively simple normalized function which is very nearly as good.

$$\varphi(1,2,3) = 8.70800g[1000] + 0.46443\{g[1010] + g[1100]\} + 3.74530\{g[1020] + g[1200]\} - 2.25446g[1110] + 4.66553g[1001] - 0.60372g[1002] - 7.76625g[0^*000] - 1.85902\{g[0^*010] + g[0^*100]\} + 1.57214f[0001] + 1.93299h[0001].$$

It will be recalled that the complete wave function is the sum of three such terms, differing by systematic permutations of the electron numbers, each multiplied by a different spin factor. Accordingly the above expression for $\varphi(1,2,3)$ has been normalized to 1/3.

The energy given by this function is as follows:

	Total energy, $R_{\mathrm{Li}}h$,	*Free ion,* $R_{\mathrm{Li}}h$,	*Ionization* (ev)
Experiment	−14.95784	−14.56160	5.364
Function	−14.95215	−14.55776	5.339
Error	0.00569	0.00384	−0.025
Percent	0.038	0.026	0.47

Of the total "polarization energy" of 0.05 ev about three-eighths comes from the pair of electrons with the same spin, and five-eighths from the other pair. This inequality is in agreement with the general rule that polarization is more important in singlet than in triplet states of two-electron systems.

Method of Calculation

The calculation of the matrix components of energy and unity hinges upon the evaluation of the integrals

$$I(abcdef/\alpha\beta\gamma) = \int dV e^{-(\alpha r_1 + \beta r_2 + \gamma r_3)} r_1^a r_2^b r_3^c r_{23}^d r_{31}^e r_{12}^f.$$

Consider first the case that d, e, f are each either 0 or -1. If e (say) is 0, then the integral is readily evaluated by taking as variables of integration r_1, r_2, r_3, $\cos\theta_{12}$, $\cos\theta_{23}$, φ_{13} (the angle between the plane containing r_1 and r_2 and that containing r_3 and r_2) and three unspecified angles giving the orientation of the whole system in space. The last four variables do not enter the integrand. We set $1/r_{23} = \Sigma_n s_{23}^n g_{23}^{-n-1} P_n(\cos\theta_{23})$ and $1/r_{12} = \Sigma_n s_{12}^n g_{12}^{-n-1} \times P_n(\cos\theta_{12})$, where s_{ij}, g_{ij} mean, respectively, the smaller and the greater of r_i, r_j. Upon integration over the cosines, the terms for $n>0$ disappear, and we have, for example,

$$I(abc-10-1/\alpha\beta\gamma) = 64\pi^3\{W_{a+2,\,b+1,\,c+1}(\alpha,\beta,\gamma) + W_{a+2,\,c+2,\,b}(\alpha,\gamma,\beta) + W_{b+2,\,a+1,\,c+1}(\beta,\alpha,\gamma) + W_{b+2,\,c+1,\,a+1}(\beta,\gamma,\alpha) + W_{c+2,\,a+2,\,b}(\gamma,\alpha,\beta) + W_{c+2,\,b+1,\,a+1}(\gamma,\beta,\alpha)\},$$

where

$$W_{f,\,g,\,h}(\alpha,\beta,\gamma) = \int_0^\infty dx \int_x^\infty dy \int_y^\infty dz x^f e^{-\alpha x} y^g e^{-\beta y} z^h e^{-\gamma z}.$$

$$I(abc-100/\alpha\beta\gamma) = 64\pi^3 A_{a+2}(\alpha)\{V_{b+2,\,c+1}(\beta,\gamma) + V_{c+2,\,b+1}(\gamma,\beta)\},$$

where

$$A_j(\alpha) = \int_0^\infty dx x^j e^{-\alpha x}$$

and

$$V_{m,\,n}(\beta,\gamma) = \int_0^\infty dy \int_y^\infty dz y^m e^{-\beta y} z^n e^{-\gamma z}.$$

We note that

$$A_j(\alpha) V_{m,\,n}(\beta,\gamma) = W_{j,\,m,\,n}(\alpha,\beta,\gamma) + W_{m,\,j,\,n}(\beta,\alpha,\gamma) + W_{m,\,n,\,j}(\beta,\gamma,\alpha).$$

If $d=e=f=-1$, it does not seem possible to find a symmetrical method of evaluating the integral. We have expanded $1/r_{13}$ as before in terms of $P_n(\cos\theta_{13})$, which, by the theorem of biaxial harmonics, can be replaced by $P_n(\cos\theta_{12})$ $P_n(\cos\theta_{23})$ plus terms which disappear upon integration over φ_{13}. We thus find

$$I(abc-1-1-1/\alpha\beta\gamma) = 64\pi^3 \Sigma_n (2n+1)^{-2} \times \{W_{a+2n+2,\,b+1,\,c-2n}(\alpha,\beta,\gamma) + W_{a+2n+2,\,c+1,\,b-2n}(\alpha,\gamma,\beta) + W_{b+2n+2,\,a+1,\,c-2n}(\beta,\alpha,\gamma) + W_{b+2n+2,\,c+1,\,a-2n}(\beta,\gamma,\alpha) + W_{c+2n+2,\,a+1,\,b-2n}(\gamma,\alpha,\beta) + W_{c+2n+2,\,b+1,\,a-2n}(\gamma,\beta,\alpha)\}.$$

The final formula is thus symmetrical, and the summation converges rapidly.

Because of our not considering individual terms in which more than one interelectronic coordinate explicitly appear, we did not encounter the case that $e>0$. (This case could, however, be readily handled by extending the following method.) By means of the relation

$$r_{23}^2 = r_2^2 + r_3^2 - 2r_2 r_3 \cos\theta_{23}$$

it is possible to reduce any case of positive d by steps of two powers of r_{12} until one reaches either $d=0$ or $d=-1$. The resulting expressions will have the same form as the integral I, except that some of them will now contain powers of $\cos\theta_{23}$ in the integrand. These can readily be treated by the methods indicated above. The same reduction applies to the case that $f>0$. It was found advantageous to work out the explicit formulas, in terms of the W's, giving $I(abcdef/\alpha\beta\gamma)$ for every set of numbers d, e, f which we required, as this resulted in considerable cancellation, and also improved the rapidity of convergence when all three numbers were odd and a summation had to be used.

The first step in the calculation is the construction of tables of the integrals A, V, and W, according to the following definitions and recurrence relations. By the systematic use of the latter, the work can be made self-checking by verifying that two independent chains of calculations, in which the relations are applied in different order, lead to the same final value.

$$A_j(\alpha)=\int_0^\infty e^{-\alpha x}x^j dx, \quad j\geqq 0.$$

$$V_{mn}(\alpha,\beta)=\int\int_{x<y} e^{-\alpha x}x^m e^{-\beta y}y^n dxdy, \quad m\geqq 0, \quad m+n\geqq -1.$$

$$W_{fgh}(\alpha,\beta,\gamma)=\int\int\int_{x<y<z} e^{-\alpha x}x^f e^{-\beta y}y^g e^{-\gamma z}z^h dxdydz,$$
$$f\geqq 0, \quad f+g\geqq -1, \quad f+g+h\geqq -2.$$

$$A_0(\alpha)=1/\alpha;$$

$$A_j(\alpha)=(1/\alpha)^j A_{j-1}(\alpha), \quad j\geqq 1.$$

$$V_{0,-1}(\alpha,\beta)=\frac{1}{\alpha}\log\frac{\alpha+\beta}{\beta};$$

$$^*V_{0,n}(\alpha,\beta)=(1/\alpha)[A_n(\beta)-A_n(\alpha+\beta)], \quad n\geqq 0;$$

$$V_{m,n}(\alpha,\beta)=(1/\alpha)[mV_{m-1,n}(\alpha,\beta)-A_{m+n}(\alpha+\beta)], \quad m\geqq 1, \quad m+n\geqq 0;$$

$$=(1/\beta)[A_{m+n}(\alpha+\beta)+nV_{m,n-1}(\alpha,\beta)], \quad m\geqq 0, \quad m+n\geqq 0;$$

$$=\frac{1}{\alpha+\beta}[mV_{m-1,n}(\alpha,\beta)+nV_{m,n-1}(\alpha,\beta)], \quad m\geqq 1, \quad m+n\geqq 0.$$

$$^*W_{0,g,h}(\alpha,\beta,\gamma)=(1/\alpha)[V_{g,h}(\beta,\gamma)-V_{g,h}(\alpha+\beta,\gamma)], \quad g\geqq 0, \quad g+h\geqq -1.$$

$$W_{f,g,h}(\alpha,\beta,\gamma)=(1/\alpha)[fW_{f-1,g,h}(\alpha,\beta,\gamma)-V_{f+g,h}(\alpha+\beta,\gamma)], \quad f\geqq 1, \quad f+g\geqq 0, \quad f+g+h\geqq -1;$$

$$=(1/\beta)[gW_{f,g-1,h}(\alpha,\beta,\gamma)+V_{f+g,h}(\alpha+\beta,\gamma)-V_{f,g+h}(\alpha,\beta+\gamma)], \quad f\geqq 0, \quad f+g\geqq 0, \quad f+g+h\geqq -1;$$

$$=(1/\gamma)[hW_{f,g,h-1}(\alpha,\beta,\gamma)+V_{f,g+h}(\alpha,\beta+\gamma)], \quad f\geqq 0, \quad f+g\geqq -1, \quad f+g+h\geqq -1;$$

$$=\frac{1}{\alpha+\beta+\gamma}[fW_{f-1,g,h}(\alpha,\beta,\gamma)+gW_{f,g-1,h}(\alpha,\beta,\gamma)+hW_{f,g,h-1}(\alpha,\beta,\gamma)], \quad f\geqq 1, \quad f+g\geqq 0, \quad f+g+h\geqq -1.$$

By reversing these recurrence relations, the functions can be computed for negative n, g, and h, within the limits for which they remain finite. It is well to avoid the relations marked,* as the computation of tables of all the W's required to construct all the I's for a given choice of α, β, γ, can then be based upon preliminary tables of $A(\alpha+\beta+\gamma)$ and of $V(\alpha,\beta+\gamma)$, $V(\beta,\alpha+\gamma)$, $V(\gamma,\alpha+\beta)$, $V(\alpha+\beta,\gamma)$, $V(\beta+\gamma,\alpha)$ and $V(\alpha+\gamma,\beta)$.

Each term in our trial series consists of two parts, but because of the symmetry of the Hamiltonian operator, the matrix elements of energy and unity between any two such terms contain but two components, each taken twice. These components are computed separately. The elements of unity need no further discussion. Those of energy are found to fall into two classes, according as the interelectronic distances specifically involved in the combining functions refer to the same or to different pairs of electrons. The first class gives rise to the integral

$$(2\kappa^3/64\pi^3)\int dV\{e^{-(\alpha'\rho_a+\beta'\rho_b+\gamma'\rho_c)}\rho_a{}^{k'}\rho_b{}^{m'}\rho_c{}^{n'}\rho_{ab}{}^{p'}\}\times H\{e^{-(\alpha\rho_a+\beta\rho_b+\gamma\rho_c)}\rho_a{}^{k}\rho_b{}^{m}\rho_c{}^{n}\rho_{ab}{}^{p}\}=\kappa^2 L+\kappa M;$$

$$L=-(\alpha^2+\beta^2+\gamma^2)I(000,000)+\alpha(2k+2+p)I(-100,000)-k(k+1+p)I(-200,000)+\beta(2m+2+p)\times I(0-10,000)-m(m+1+p)I(0-20,000)+\gamma(2n+2)I(00-1,000)-n(n+1)I(00-2,000)+p\{-(m+k+2+2p)I(000,00-2)-\alpha I(-120,00-2)+\alpha I(100,00-2)+kI(-220,00-2)-\beta I(2-10,00-2)+\beta I(010,00-2)+mI(2-20,00-2)\}.$$

$$M=I[000,-100]+I[000,0-10]+I[000,00-1]-3I[-100,000]-3I[0-10,000]-3I[00-1,000].$$

In these formulas, $I[uvw, xyz]$ is an abbreviation for

$$I[k+k'+u, m+m'+v, n+n'+w, x, y, p+p'+z/\alpha+\alpha', \beta+\beta', \gamma+\gamma'].$$

The second class of combinations produces the integral

$$(2\kappa^3/64\pi^3)\int dV\{e^{-(\alpha'\rho_a+\beta'\rho_b+\gamma'\rho_c)}\rho_a{}^{k'}\rho_b{}^{m'}\rho_c{}^{n'}\rho_{ab}{}^{p'}\}\times H\{e^{-(\alpha\rho_a+\beta\rho_b+\gamma\rho_c)}\rho_a{}^{k}\rho_b{}^{m}\rho_c{}^{n}\rho_{bc}{}^{p}\}.$$

The value of this integral is represented by the same formula as before, provided that $I[uvw, xyz]$ is now understood to be an abbreviation for

$$I[k+k'+u, m+m'+v, n+n'+w, p'+x, y, p+z/\alpha+\alpha', \beta+\beta', \gamma+\gamma'].$$

These formulas are not symmetrical; the coefficients of the I's are determined solely by one of the combining functions. This is in practice rather an advantage, since it provides two different methods of calculating the components, and thereby checking the rather treacherous step of picking out the coefficients. A symmetrical formula could, if desired, be worked out by a method which we have discussed in a previous paper.[8] The same paper contains a description of the process of setting up and solving the secular equation, and thereby determining the best function which can be constructed from a given selection of terms.

Choice of Parameters and Terms

It would be desirable to have a form of trial function permitting independent variation of the screening constants for the inner and outer electrons, but this degree of flexibility could not be combined with that secured by the use of many terms with adjustable coefficients without tremendously multiplying the labor of computation. With our definition of the trial function, the screening parameters are $s_1=\kappa\delta$ for the inner and $s_2=\kappa\gamma$, $s_2{}^*=\kappa\gamma^*$ for the outer orbital. The only practicable variation, that of κ, changes all three in the same ratio. It is therefore important to start with suitable ratios of δ, γ, and γ^*, and this can most easily be accomplished by making them equal to the values which s_1, s_2, and $s_2{}^*$ are expected to have, relying upon variation in κ only for slight additional improvement. Accordingly, γ and γ^* were fixed by rounding off Wilson's values, taking $\gamma=0.65$, $\gamma^*=1.5$. To fix δ, we investigated the energy of the ion as given by a six-term function similar to F of Table I but with variable screening parameter. Table II contains the results, which indicate that

[8] H. M. James and A. S. Coolidge, J. Chem. Phys. 1, 825 (1933).

TABLE II. *Computed energy of Li^{++}, as function of screening constant s_1.*

s_1	Ion Energy, $R_{Li}h$	Error (ev)	s_1	Ion Energy, $R_{Li}h$	Error (ev)
2.7	−14.55844	0.043	3.0	−14.55776	0.052
2.85	−14.55850	0.042	3.24	−14.55452	0.096

$s_1 = 2.79$ is the best value, and would give an energy error of 0.041 ev, or 0.020 percent, to be compared with the 0.014 percent error in Hylleraas' treatment of He, in which the same six terms were used. However, when many terms in the series are present, readjustment among the coefficients takes care of considerable variations in the screening constant, which therefore need not be very carefully chosen. We selected $\delta = 3$ for ease in computing. A smaller value would have improved our total energy by 0.011 ev, but, in view of the results already presented, would not have affected our ionization energy appreciably.

With δ, γ, and γ^* so fixed, the effect of taking κ different from 1 can be anticipated. The outer orbital will be directly influenced by the change in s_2 and s_2^*, but since we have already chosen practically the best values for these constants, this will cause but a second-order change in the ionization energy. A poor choice of γ and γ^* could have been to a large degree corrected by varying κ. The effect on the core function of such a variation will be small, owing to readjustment of coefficients, and the residual effect will not be large enough sensibly to alter the ionization energy. We conclude that, so far as ionization energy is concerned, the chief usefulness of the variable κ is to correct errors in choice of γ and γ^*, and that in our case little gain could be expected. We have verified these relations by calculations with a single-term L orbital, for which our γ is not the best value of s_2.

In selecting terms, we first set up a function for the ion, using the terms occurring in Hylleraas' function for the analogous ground state of He. Upon multiplying these by the main term of the L orbital, $re^{-s_2 r}$, we obtain the six terms $g[1000]$, $g[1010]+g[1100]$, $g[1020]+g[1200]$, $g[1110]$, $g[1001]$, and $g[1002]$, the best combination of which gives an ionization energy error of 0.093 ev ($F-P$ combination, Table I). To these terms there correspond six "star" terms, $g[0*000]$, $g[0*010]+g[0*100]$, etc., arising from the minor term $e^{-s_2^* r}$ in the L orbital. From analogy with results with core function E, we should expect that inclusion of these terms would reduce the error to −0.056 ev. It was actually found that the first two star terms alone sufficed to carry us within 0.005 ev of this value, and we did not go to the labor of computing the matrix elements required for the remaining terms. We did find that inclusion of the additional terms $g[2000]$ and $g[1*000]$ produced an improvement of 0.006 ev, leaving an error of −0.055 ev. This improvement is clearly due to perfecting the L orbital; it is exactly the same as was found with the crude core function C upon going from orbital Q to the best combination of six terms, which is a rather striking example of the degree to which corrections for different sorts of defects in the function are additive, and supports our conclusion that the ionization energy error for the best separate-shell function is −0.050 ev.

To take account of inter-shell polarization, we included the following additional terms: $f[0001]$, $f[1001]$, $f[0*001]$, $h[0001]$, $h[0011]+h[0101]$, $h[1001]$, and $h[0*001]$. The writers' discussion[5] of the most desirable form for polarization terms, when applied to this case, suggests the usefulness of $f[0001]$ and $h[0001]$, or modifications of these terms in which γ is somewhat increased. These are, indeed, the most helpful of the above terms. The terms $f[1001]$ and $h[1001]$, use of which would correspond to taking account of polarization by introducing the factor $(1+cr_{ij})$, are almost completely without value. However, as is also suggested by the argument just referred to, when $I[2000]$ is included in the function these terms are of some service, though not as helpful as the more compact $f[0001]$ and $h[0001]$. More compact even than these terms—indeed, apparently somewhat too compact—are $f[0*001]$ and $h[0*001]$. When correlated with $g[1*000]$ these terms are less useful than $f[0001]$ and $h[0001]$, but not so poor as the other terms. As one would expect from the fact that none of the polarization terms are ideal in character, an appreciable further improvement is obtained by including all of them in the function.

All the above polarization terms were constructed from the principal term of the core function. In order to check that polarization could be satisfactorily treated in this way we introduced into the most complicated of our functions the term $h[0011]+h[0101]$, which corresponds to the important term $h[0001]$ in the treatment of the polarization, but is constructed on another term of the core function. Table I shows that this addition would markedly improve the representation of the core in connection with the polarization effect, yet the computed energy of the system is improved by just 0.001 ev. The introduction of other polarization terms of this type is apparently unnecessary.

On the Constant A in Richardson's Equation

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According to Herzfeld, the "chemical constant" of the electron gas is different in the high temperature region, where all actual measurements are carried out, from its value at very low temperatures. Hence the value of the constant A in Richardson's equation must be different at high temperatures from the well-known low temperature value of 120 amp./cm² °K². The present paper gives a calculation of the high temperature value in terms of thermodynamic quantities and a numerical estimation of these.

1

IT is well known that the constant A in Richardson's formula[1] for the thermionic current i

$$i = AT^2 e^{-W/RT} \tag{1}$$

(W is the measured work function) should have under ideal conditions the value 120 amp./cm² °K². Under "ideal conditions" we mean that:

(a) The reflection coefficient r for electrons should be zero, i.e., all electrons striking the surface should be absorbed by the same.

(b) The work function W should be constant. The work function is defined as the energy necessary to remove one electron from the top of the Fermi distribution and bring it to a point near the surface, but still to a distance from it which is large as compared with the lattice constant. The "top of the Fermi distribution" again means the energy of that electron which has the highest energy if all electrons are in the lowest possible state. This is the work function which is measured experimentally by the photoelectric effect if Fowler's method[2] is used for the evaluation.

(c) That the electron gas in free space should behave like an ideal gas.

(d) Finally, the surface must be uniform and thus free from patches and contaminations.

This last condition and its effects have been carefully analyzed by J. A. Becker.[3] It seems that it can account in the case of the most careful experiments, and for low accelerating potentials for small deviations of A from 120 only, and generally only for a lowering of this value. Under the conditions (a)–(d), (1) is a consequence of the principle of detailed balance and general quantum statistical laws.[4]

Condition (c) is fulfilled for not too high temperatures[5] and will be assumed further on. If the reflection coefficient is different from zero, we should only expect an additional coefficient $1-r$ in (1). Since $1-r$ is certainly in the order of magnitude of 1 and smaller than this, the reflection can explain only a deviation of A from 120 by such a factor.[6] In spite of this, the experimental values[7] are in most cases rather far from 120. It must be emphasized, however, that these experimental values are still subject to comparatively large variations and in many cases hardly reproducible. They are most trustworthy if the work function is measured photoelectrically also. It is only too common an experience that a new set of experiments changes the measured values of both A and W considerably, generally both in the same direction, which indicates that not so much the measurement of i, as that of its temperature coefficient, is crucial. In spite of this, it is generally accepted[8]

[1] For the history of Richardson's discovery cf., e.g., W. Schottky, *Handbuch der Experimentalphysik*, Vol. XIII (Leipzig, 1928), or A. L. Reimann, *Thermionic Emission* (London, 1934).

[2] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

[3] J. A. Becker, Rev. Mod. Phys. **7**, 95 (1935).

[4] Cf. reference 1 and K. F. Herzfeld, Phys. Rev. **35**, 248 (1930), also J. H. Becker and W. H. Brattain, Phys. Rev. **45**, 694 (1934).

[5] Cf. M. v. Laue, *Jahrbuch der Radioaktivität und Elektronik*, Vol. 15, 205, etc. (1918) and W. Schottky, reference 1.

[6] L. Nordheim, Zeits. f. Physik **46**, 833 (1928); Proc. Roy. Soc. **A121**, 626 (1928); R. H. Fowler and L. Nordheim, Proc. Roy. Soc. **A119**, 173 (1928) show that the reflection coefficient is very small in general, around 0.07. See also Langmuir and Jones, Phys. Rev. **31**, 401 (1928).

[7] Cf. A. L. Reimann, reference 1 and A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (New York, 1932). For Cb, H. B. Wahlin and L. O. Sordahl, Phys. Rev. **45**, 886 (1934), for Rh unpublished data of H. B. Wahlin.

[8] I am much indebted to Professor L. A. DuBridge for a discussion on this point. Cf. also his monograph, *Actualités Scientifiques et Industrielles*, No. 268, Paris, 1935.

TABLE I. *Measured values of the constants in Richardson's equation.*

	A	W		A	W
Cs	162	1.81	Ta	60	4.12
Ba	60	2.11	Hf	14.5	3.53
Ni	1,380	5.02	Th	70	3.38
Pd	60	4.98	Re	200	5.1
Pt	17,000	6.27	Cu?	65	4.33
Mo	55	4.15	Ag?	0.76	3.56
W	60	4.53	Au?	40	4.32
Zr	330	4.12	Cb	57	3.96
			Rh	35	4.81

that the deviations of A from 120 are real and must be explained by the breakdown of assumption (b). The present paper will be devoted to a discussion of (b).

2

The consequences of the temperature variation of the work function have often been analyzed,[9] especially by Bridgman and Herzfeld. I shall follow the latter's treatment quite closely. The reason this subject is taken up again, is that our somewhat improved knowledge of the metallic structure allows a somewhat closer analysis which shows that in addition to the effect, analyzed by Herzfeld (which is reproduced), there is another effect which tends to compensate for it in many cases. This is the reason, perhaps, that the measured A's are not all higher than 120, as one may expect from Herzfeld's paper.

It has been emphasized by Becker and Brattain[10] that the quantities measured in case of variable work function (and thus contained in Table I) are W^* and A^*, defined by

$$W^* = RT^2(d/dT)\ln i/T^2,$$

$$\ln A^* = \ln i/T^2 + T(d/dT)\ln i/T^2 = \ln i/T^2 + W^*/RT, \tag{2}$$

where i is the thermionic current.

The procedure to obtain theoretical expressions for W^* and A^* is to calculate first i and obtain then W^* and A^* by (2).

3

In order to calculate the current, one may first calculate the vapor pressure P of the electron gas at a point with zero electrostatic potential by thermodynamics. If P is given, the number of electrons striking the surface can be calculated by elementary kinetic theory (m is the electronic mass) to be $P/(2\pi mkT)^{\frac{1}{2}}$. If r is the reflection coefficient, this gives a current i per cm^2 of the metal.

$$i = Pe(1-r)/(2\pi mkT)^{\frac{1}{2}}. \tag{3}$$

The current from the metal is equal to this in equilibrium and is supposed to be equal also under the conditions of thermionic emission. Thus the problem reduces to the calculation of the vapor pressure P.

Both the vapor pressure and the work function[11] depend, in addition to the temperature T, on the (mechanical) pressure p, under which the metal is kept. We shall assume that the metal carries always only an infinitesimally small charge only. If we allow ϵ electrons per mole of metal to escape and keep the volume of the metal constant, the mechanical pressure will increase by $\epsilon p_v(v, T)$. The energy necessary for the removal of ϵ electrons, when the metal is kept at constant volume, is $\epsilon W_v(v, T)$. It seems to be simplest to apply the Clausius Clapeyron cycle by keeping the metal at constant volume. We then have[12]

$$\partial \ln P(v, T)/\partial T = W_v(v, T)/RT^2 + 5/2T, \tag{4}$$

which gives

$$\ln P(v, T) = -\frac{W_v(v, 0)}{RT} + (5/2)\ln T + j + \int_0^T [W_v(v, \tau) - W_v(v, 0)]\frac{d\tau}{R\tau^2}$$
$$j = (3/2)\ln(2\pi mk/h^2) + \ln 2. \tag{5}$$

The well-known Sackur-Tetrode value of the chemical constant must be increased by ln 2 because of the spin. In order to determine p_v, we can apply the usual cycle to a piece of metal

[9] P. W. Bridgman, Phys. Rev. **31**, 90 (1928); K. F. Herzfeld, reference 4.

[10] Reference 4.

[11] For the definition of the work function see the preceding section. The vapor pressure P is a function of the mechanical pressure p for ordinary vaporization also, but this effect is rarely considered.

[12] In this section, temperature T and volume v will be the independent variables. Thus temperature derivatives are always to be taken at constant volume, volume derivatives at constant temperature.

which is deprived of ϵ electrons permole. The pressure is $p+\epsilon p_e$, the energy $E+\epsilon W_e$, so that we have

$$\frac{\partial E}{\partial v}+\epsilon\frac{\partial W_e}{\partial v}+p+\epsilon p_e=T\frac{\partial}{\partial T}(p+\epsilon p_e), \quad (6)$$

which gives in addition to the usual

$$\partial E/\partial v+p=T\partial p/\partial T \quad (7)$$

valid for any substance, the required

$$\partial W_e/\partial v+p_e=T\partial p_e/\partial T \quad (8)$$

since (6) holds for every ϵ. From (8) follows

$$p_e=-\frac{\partial W_e(v,0)}{\partial v}+T\int_0^T\left[\frac{\partial W_e(v,\tau)}{\partial v}-\frac{\partial W_e(v,0)}{\partial v}\right]\frac{d\tau}{\tau^2}. \quad (9)$$

We shall now calculate W^* and A^* by (5), (3) and (2). We have to remember, for this, that when the thermionic current is measured at different temperatures, not the volume, but the mechanical pressure of the metal is kept at constant value, namely zero. The temperature derivatives in (2) are meant to be taken at constant pressure, therefore. Hence, if α is the volume expansion coefficient, v_0 the molal volume, we have

$$W^*=RT^2\left(\frac{\partial}{\partial T}+v_0\alpha\frac{\partial}{\partial v}\right)\ln\frac{i}{T^2}$$

$$=RT^2\left(\frac{\partial}{\partial T}+v_0\alpha\frac{\partial}{\partial v}\right)\ln\frac{P}{T^{5/2}} \quad (10)$$

or

$$W^*=W_e(v,T)+v_0\alpha Tp_e \quad (11)$$

as the comparison with (9) shows. For A^*, we have

$$\ln(A^*/A(1-r))=-W_e(v,0)/RT+W_e(v,T)/RT+\int_0^T[W_e(v,\tau)-W_e(v,0)](d\tau/R\tau^2)+v_0\alpha p_e/R. \quad (12)$$

Here A is the constant for the ideal case, 120 amp. cm^{-2} °K^{-2}. The last term in (12) is that of Herzfeld, the other ones have been omitted by him, since the work function chiefly depends on the volume. Its contribution to A^* is not negligible, however. In general, p_e is negative, the pressure decreases if an electron is removed.

4

For the evaluation of (12) we shall make assumptions very similar to those of Herzfeld. The total energy of the metal contains two parts. The first, $V(v)$ arises from the motion of the electrons, depending, therefore, on the volume only.[13] The second arises from the motion of the nuclei. The first part is the most important for the actual value of the work function, its change by the removal of electrons from the metal gives practically all of this quantity. For the second part, an expression $RTD(\Theta/T)$ will be used. In this, Θ is a function of the volume and will be changed also by the removal of electrons by the amount $\epsilon\Theta_e$ if ϵ electrons per mole are removed. The total energy of a mole of the metal, out of which ϵ electrons have been removed and brought to a point near the surface but still sufficiently distant from it in order to make the image force negligible, is thus

$$E(v,T)+\epsilon W_e(v,T)=V(v)+\epsilon W_e(v,0)+RTD(\Theta/T)+\epsilon R\Theta_e D'(\Theta/T). \quad (13)$$

These assumptions can be justified on the basis of the usual assumption of fast electronic and slow nuclear motion,[14] but I shall not enlarge upon this subject. From (13) one readily obtains

$$W_e(v,T)=W_e(v,0)+R\Theta_e D'(\Theta/T), \quad (14)$$

which gives with (12)

$$\ln\frac{A^*}{A(1-r)}=\frac{\Theta_e}{T}D'\left(\frac{\Theta}{T}\right)+\Theta_e\int_0^T D'\left(\frac{\Theta}{\tau}\right)\frac{d\tau}{\tau^2}+\frac{v_0\alpha p_e}{R}$$

$$=(\Theta_e/T)D'(\Theta/T)-(\Theta_e/\Theta)D(\Theta/T)+v_0\alpha p_e/R,$$

$$\ln(A^*/A(1-r))=-C_v\Theta_e/R\Theta+v_0\alpha p_e/R=-3\Theta_e/\Theta+v_0\alpha p_e/R, \quad (15)$$

[13] We shall neglect the small specific heat of free electrons (cf. A. L. Reimann, reference 1).

[14] Cf., e.g., H. Pelzer and E. Wigner, Zeits. f. physik. Chemie **B15**, 445 (1932); F. London, Zeits. f. Physik **74**, 143 (1932).

where $C_v \approx 3R$ is the specific heat of the metal at constant volume, it has assumed its classical value at the temperatures under consideration.

The thermionic emission can be considered as a generalized dissociation reaction, and calculated, hence, according to the transition state method for calculating reaction rates.[15] The result is identical with the one obtained here, but I preferred this method because it is the more usual one in these problems. As has been remarked by Herzfeld, (15) corresponds to the expression for the chemical constant of the electron gas at high temperatures, while the familiar 120 amp./°K² cm² is the low temperature expression. This is quite similar to the situation for H_2, e.g.: at low temperatures the chemical constant is $(3/2)\ln(2\pi mk^{5/3}/h^2)$ while at high temperatures there is an additional $\ln 8\pi^2 kJ/h^2$. In contrast to H_2, the change of the "chemical constant" in our case is due to a change in the condensed state. Also the temperature dependence does change in H_2 (from $T^{5/2}$ to $T^{7/2}$) while there is no such change in our case.

5

Next we shall try to estimate the quantities Θ_e and p_e occurring in (15). It must be remarked at the outset that these two quantities are of a rather different nature: Θ_e is a function of the volume only, but p_e depends, according to (9), on the temperature and can be reduced to the more basic quantities, $\partial W_v(v, 0)/\partial v$, Θ_e and $d\Theta_e/dv$ by (14). One obtains thus

$$\ln(A^*/A(1-r)) = -C_v\Theta_e/R\Theta - (v_0\alpha/R)\partial W_v(v, 0)/\partial v - v_0\alpha T(\partial/\partial v)(C_v\Theta_e/R\Theta) \quad (16)$$

since the integral in (9) is just the v derivative of the expression we have calculated in the previous section.

[15] For the history of this method cf. E. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935). The formula

$$i = AT^2 e^{-w/RT} \quad (*)$$

used by J. A. Becker and W. H. Brattain (reference 4) has been derived in the papers to which they take reference only for the case when the work function is independent of temperature. Of course, it is always possible to represent the thermocurrent by a formula (*) with variable w, but this w will not be equal to the work function. It follows furthermore from the third law that w can have no term linear in T at low temperatures (cf. reference 9).

It would be rather difficult to estimate the last expression in (16) since it contains $d\Theta_e/dv$. If one assumes however, that $v(\partial/\partial v)(C_v\Theta_e/R\Theta)$ is of the order of magnitude of $C_v\Theta_e/R\Theta$ itself—which seems reasonable, the last term can be neglected altogether, because $\alpha T = 10^{-2}$. Since $W_v(v, 0)$ is the energy necessary at the absolute zero, to remove one electron, $\partial W_v(v, 0)/\partial v$ is the negative increase in pressure, due to the removal of one electron. Since the electrons do the binding in the metal, the removal of one will loosen the binding and the actual pressure decrease will not be quite as great as calculated on the free electron hypothesis. For alkalis, one can obtain an estimate of this magnitude from the formulas, derived for the calculation of the work function.[16] Our $W_v(v, 0)$ is in the present approximation what is denoted there by φ. Eq. (7) reference 16 reads in our notation:

$$-W_v(v, 0) = 13.5(E_0 + 5\cdot 2.21/3r_s^2 + 1.18/r_s - 0.58/(r_s+5.1) - 0.19r_s/(r_s+5.1)^2 - eD). \quad (17)$$

The work function is expressed here in volts, r_s in Bohr's units ($0.528\cdot 10^{-8}$ cm) and is defined by $4\pi r_s^3/3 = v_0/L$ = atomic volume. D is the momentum of the double layer on the surface and will be neglected hereafter. From (17) we obtain

$$v_0\partial W_v/\partial v = (r_s/3)\partial W_v/\partial r_s = -4.5(r_s dE_0/dr_s - 7.4/r_s^2 - 1.18/r_s + 0.58r_s/(r_s+5.1)^2 + 0.38r_s^2/(r_s+5.1)^3). \quad (18)$$

In order to eliminate dE_0/dr_s, we set the derivative of (8) reference 16 equal to zero. This expresses that the total energy is a minimum for r_s.

$$-r_s dE_0/dr_s + 4.42/r_s^2 + 0.28/r_s - 0.58r_s/(r_s+5.1)^2 = 0. \quad (19)$$

This gives

$$v_0\partial W_v(v, 0)/\partial v = 4.5(3/r_s^2 + 0.9/r_s - 0.38r_s^2/(r_s+5.1)^3), \quad (20)$$

which is for $r_s = 4$ about 1.5 volts. The second term in (16) thus becomes with $\alpha = 21.10^{-5}$ about -3.6.

[16] J. Bardeen and E. Wigner, Phys. Rev. **48**, 84 (1935).

The quantity Θ_e/Θ is the percent change of the vibration frequencies for one percent change in the number of electrons. It is, therefore, half the percent change of the restoring force F, if one percent of the electrons is removed.

In order to obtain an estimate for this, we may consider first the whole restoring force if only one ion is displaced. This is the force which acts on the displaced ion and originates from the electron cloud which is itself distorted by the displacement of the ion.

It is difficult, in general, to calculate the distortion of the electron clouds. Naturally, the inner electrons can be considered to be rigidly attached to the ion. We may assume that the valence electrons have an even distribution throughout the lattice and show wriggles in the neighborhood of the ion only. Then, the total charge distribution of the valence electron can be considered to contain two parts: ρ_1, the variations of which are appreciable only in distances comparable with the lattice constant, and ρ_2 which contains the small wriggles only. It seems reasonable to assume that the ion carries the wriggles with itself but as long as only one ion is displaced, the slowly varying part of the charge will not be much affected. If the ion was displaced by x in the X direction, it will be acted upon by a force

$$Fx = xZe\partial E_x/\partial x, \tag{21}$$

where E is the field due to the slowly varying part ρ_1 of the electronic charge and Ze the ionic charge. We have, by Poisson's equation div $E = 4\pi\rho_1$ and for a cubic lattice, this gives because of $\partial E_x/\partial x = \partial E_y/\partial y = \partial E_z/\partial z$

$$F = 4\pi\rho_1 Ze/3. \tag{22}$$

The percent change of this,[17] for a one percent decrease of the number of electrons is simply $-\rho_{1t}/\rho_{1m}$ where ρ_{1t} is the slowly varying part of the density of the highest energy electrons, at the point where the ion is; ρ_{1m} is the mean value of the same quantity for all valence electrons. The first term of (16) is therefore, approximately

$$(3/2)(\rho_{1t}/\rho_{1m}). \tag{23}$$

This will be comparatively large (~ 1.5), if the last valence electron is an s electron, small otherwise. If the highest energy electron happens to be such an electron in the lattice, for which ρ_{1t} is zero, the whole first term will be negative also, because of the approximations we made.

6

It is hardly necessary to mention that while the considerations of sections 2 and 3 are, (12) inclusive, strictly based on thermodynamics and those of 4 also should be correct within a very small error, the considerations of section 5 are very crude and will not give, in general, more than the sign of the effects and their order of magnitude. What can be claimed safely, is only

(a) that it is purely accidental if the constant A^* in Richardson's equation (defined by (2)) has the value 120 amp./°K² cm² sec.

(b) that the deviation in the ln of A^* should be of the order of magnitude 1–3, rather negative than positive. It should be negative always when the last valence electron is not essentially an s electron in the lattice.

It should be emphasized once more that rather large deviations in the constant A^* can be caused by a patchy character of the surface, as considered by Becker and Rojansky.[3] These patches can consist in surface contamination or also in the polycrystalline character of the surface, since different crystal planes will have different work functions. It would be desirable, from this point of view, to measure the work function and A^* on definite crystal planes, i.e., to use single crystals for the experiments.[18]

In some cases, zero energy outside of the metal may correspond to a forbidden region inside. This would have as consequence an unusually large reflection coefficient.[19] The effect of a reflection coefficient has also been omitted in this paper.

It is a pleasure to express my gratitude to Professor Herzfeld for his valuable discussion and criticism of this paper.

[17] One can calculate, from (22), the characteristic temperature of the metal, and it comes out in the right order of magnitude. A more satisfactory calculation of the vibrational frequencies of a metal has been given lately by K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936).

[18] Professor H. B. Wahlin has pointed out to me that part of the effect of the continued heating and flashing of the samples is perhaps due to recrystallization. Cf. H. B. Wahlin and J. A. Reynolds, Phys. Rev. **48**, 751 (1935).

[19] P. M. Morse, Phys. Rev. **35**, 1310 (1930).

The Transformation of Reference Systems in the Page Relativity

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(Received March 16, 1936)

1

IN his paper, *A New Relativity*, Page[1] introduces reference systems of particle observers where the comparison of times and the measurement of distances are based solely on geometrical optics. Hence, by means of optical experiments, two such systems will be indistinguishable if suitable coordinates (x, y, z, t) can be introduced for the observers of each system such that light travels along straight lines with constant speed and the space coordinates (x, y, z) are Cartesian coordinates of a Euclidean space. These properties are preserved by Lorentz transformations. Page considered the question of the existence of such reference systems which are not Lorentz transforms of one another. He answered the question in the affirmative by constructing systems with elements having constant acceleration with respect to an original inertial system. He also proposed the problem of investigating other types of such systems and the present paper contains the determination of all these. It is further shown that the assumption of constant light velocity plus the existence of one reference system with straight light paths implies the straightness of light paths in all such systems.

2

Consider two reference systems S and S' of the above type. A correspondence is obtained between S and S' as follows. To each particle observer P and time t in S we associate the incident particle observer P' at the time t' in S'. We consider the four dimensional space-time manifolds (x, y, z, t) and (x', y', z', t') describing the observers in S and S'. The above correspondence may then be written

$$\begin{aligned} x'&=\phi_1(x, y, z, t), \quad z'=\phi_3(x, y, z, t), \\ y'&=\phi_2(x, y, z, t), \quad t'=\phi_4(x, y, z, t). \end{aligned} \tag{T}$$

We introduce the vector notation $\mathbf{x}=(x, y, z, t)=(x_1, x_2, x_3, x_4)$. The scalar product $\mathbf{a}\cdot\mathbf{b}$ of two vectors $\mathbf{a}$ and $\mathbf{b}$ is defined as

$$\mathbf{a}\cdot\mathbf{b}=a_1b_1+a_2b_2+a_3b_3-c^2a_4b_4.$$

The light paths in S are of the form $\mathbf{x}=\mathbf{a}+\lambda\mathbf{b}$ where $\mathbf{a}$ is a vector from the origin to a point on the path, $\mathbf{b}$ is an "isotropic" vector, i.e., $\mathbf{b}\cdot\mathbf{b}=0$, and λ is a real parameter. Our problem is to completely characterize (T) under the hypothesis of constant light velocity, i.e., all light paths $\mathbf{a}+\lambda\mathbf{b}$, $\mathbf{b}\cdot\mathbf{b}=0$ in S are carried into isotropic curves in S', i.e., curves for which

$$d\mathbf{x}\cdot d\mathbf{x}=dx^2+dy^2+dz^2-c^2dt^2=0.$$

We may reduce the problem to known results by the theorem:

If all light paths $\mathbf{x}=\mathbf{a}+\lambda\mathbf{b}$ *in* S *are carried into isotropic curves by* (T), *then* (T) *leaves the differential equation* $dx^2+dy^2+dz^2-c^2dt^2=0$ *invariant.*

For since (T) carries $\mathbf{a}+\lambda\mathbf{b}$ into an isotropic curve for all $\mathbf{b}\cdot\mathbf{b}=0$, on substitution in (T) we see that

$$\sum_{i=1}^{3}\left(\sum_{j=1}^{4}\frac{\partial\phi_i}{\partial x_j}b_j\right)^2-c^2\left(\sum_{j=1}^{4}\frac{\partial\phi_i}{\partial x_j}b_j\right)^2=0. \tag{1}$$

But $d\mathbf{x}$ is an isotropic vector if $\mathbf{x}(\lambda)$ is an isotropic curve. Hence, replacing b_j in (1) by dx_j we obtain $d\mathbf{x}'\cdot d\mathbf{x}'=0$, or the transform $\mathbf{x}'(\lambda)$ of any isotropic curve $\mathbf{x}(\lambda)$ is isotropic.

The problem is thus reduced to that of determining all transformations which preserve $dx^2+dy^2+dz^2-c^2dt^2=0$. If we allow the coordinates to vary over a complex domain, t may be replaced by $(-1)^{\frac{1}{2}}(\tau/c)$ and the problem becomes that of determining the transformations which leave $dx^2+dy^2+dz^2+d\tau^2=0$ invariant. All such transformations were given by Lie[2] who showed that they are all conformal transformations and form a group depending on 15 parameters. He further showed that this group is generated by the orthogonal transformations which carry the expression $(x-x_1)^2+(x-x_2)^2+(x-x_3)^2+(x-x_4)^2$ into a constant multiple of itself, and the trans-

[1] Leigh Page, *A New Relativity*, Phys. Rev. **49**, 254 (1936).

[2] S. Lie, *Theorie der Transformationsgruppen* (Leipzig, 1893).

formations by reciprocal radii. The latter have, of course, singular points which are carried to infinity. In the following paragraph we consider properties of the analog of these reciprocal radii transformations.

3

The analog of the transformation by reciprocal radii is

$$\mathbf{x}' = P_0(\mathbf{x}) = \mathbf{x}/(\mathbf{x}\cdot\mathbf{x}). \tag{2}$$

This transformation is valid for all elements (x, y, z, t) which are not on a light path through the origin. The effect of (2) on the direction $d\mathbf{x}/d\lambda$ of a tangent to a curve $\mathbf{x}=\mathbf{x}(\lambda)$ is given by

$$\frac{d\mathbf{x}'}{d\lambda} = \frac{d}{d\lambda}\left(\frac{\mathbf{x}}{\mathbf{x}\cdot\mathbf{x}}\right) = \frac{1}{(\mathbf{x}\cdot\mathbf{x})^2}\left[(\mathbf{x}\cdot\mathbf{x})\frac{d\mathbf{x}}{d\lambda} - 2\mathbf{x}\left(\mathbf{x}\cdot\frac{d\mathbf{x}}{d\lambda}\right)\right]. \tag{3}$$

In particular, if $\mathbf{x}=\mathbf{x}(\lambda)$ is a light path not through the origin we have $\mathbf{x}(\lambda)=\mathbf{a}+\lambda\mathbf{b}$, $\mathbf{b}\cdot\mathbf{b}=0$. Hence $d\mathbf{x}/d\lambda=b$ and

$$\frac{d\mathbf{x}'}{d\lambda} = \frac{1}{(\mathbf{x}\cdot\mathbf{x})^2}[(\mathbf{x}\cdot\mathbf{x})\mathbf{b} - 2\mathbf{x}(\mathbf{x}\cdot\mathbf{b})] = \frac{1}{(\mathbf{x}\cdot\mathbf{x})^2}[(\mathbf{a}\cdot\mathbf{a})\mathbf{b} - 2\mathbf{a}(\mathbf{a}\cdot\mathbf{b})].$$

Since the vector factor on the right is independent of λ the direction of the tangent is a constant and we have the theorem:

The image of a light path is a straight line.

The speed of an element described by the four-dimensional curve $\mathbf{x}=\mathbf{x}(\lambda)$ is c if and only if $(d\mathbf{x}/d\lambda)\cdot(d\mathbf{x}/d\lambda)=0$. That the velocity of light is constant follows simply. However it is convenient to calculate $(d\mathbf{x}'/d\lambda)\cdot(d\mathbf{x}'/d\lambda)$. We obtain

$$\frac{d\mathbf{x}'}{d\lambda}\cdot\frac{d\mathbf{x}'}{d\lambda} = \frac{1}{(\mathbf{x}\cdot\mathbf{x})^4}\left[(\mathbf{x}\cdot\mathbf{x})\frac{d\mathbf{x}}{d\lambda} - 2\mathbf{x}\left(\mathbf{x}\cdot\frac{d\mathbf{x}}{d\lambda}\right)\right] \cdot \left[(\mathbf{x}\cdot\mathbf{x})\frac{d\mathbf{x}}{d\lambda} - 2\mathbf{x}\left(\mathbf{x}\cdot\frac{d\mathbf{x}}{d\lambda}\right)\right] = \frac{1}{(\mathbf{x}\cdot\mathbf{x})^4}\left(\frac{d\mathbf{x}}{d\lambda}\cdot\frac{d\mathbf{x}}{d\lambda}\right). \tag{4}$$

As an immediate consequence of (4) we conclude not only that the velocity of light is constant and that isotropic lines are preserved but the validity of the theorem:

The quotient of two physical intervals $(d\mathbf{x}\cdot d\mathbf{x})/(d_1\mathbf{x}\cdot d_1\mathbf{x})$ *is invariant.*

Lie asserts that the transformations P_0 together with the Lorenz transformations generate all the required transformations. We shall describe this result more explicitly in the next paragraph.

4

In this paragraph we give the results of Lie in a form which is directly applicable. We combine P_0 with the translations

$$\mathbf{x}' = \frac{\mathbf{x}-\mathbf{a}}{(\mathbf{x}-\mathbf{a})\cdot(\mathbf{x}-\mathbf{a})} = P_a(\mathbf{x}),$$

which are valid for all elements not on a light path from $\mathbf{a}$, and obtain

$$C_a(\mathbf{x}) = P_aP_0(\mathbf{x}) = \left[\frac{\mathbf{x}}{\mathbf{x}\cdot\mathbf{x}}-\mathbf{a}\right]\Big/\left[\left(\frac{\mathbf{x}}{\mathbf{x}\cdot\mathbf{x}}-\mathbf{a}\right)\cdot\left(\frac{\mathbf{x}}{\mathbf{x}\cdot\mathbf{x}}-\mathbf{a}\right)\right].$$

By a simple calculation it is seen that

$$C_a(\mathbf{x}) = \frac{\mathbf{x}-\mathbf{a}(\mathbf{x}\cdot\mathbf{x})}{1+(\mathbf{a}\cdot\mathbf{a})(\mathbf{x}\cdot\mathbf{x})-2(\mathbf{a}\cdot\mathbf{x})}.$$

Hence C_0 is the identity. The singular points for these transformations, i.e., the points for which the denominator is zero, form a hyperplane if $\mathbf{a}\cdot\mathbf{a}=0$, otherwise a quadratic surface. It can be shown that these singular manifolds are different if $\mathbf{a}$ and $\mathbf{b}$ are distinct. Let us suppose that $\mathbf{x}'=L(\mathbf{x})$ is a Lorentz transformation or proportional to one. It is known that: (1) $L(\mathbf{x})$ has no singular points, (2) straight lines are preserved, (3) $\mathbf{x}\cdot\mathbf{x}$ is preserved except for a constant factor. Hence all transformations LC_a preserve the differential equation $d\mathbf{x}\cdot d\mathbf{x}=dx^2+dy^2+dz^2-c^2dt^2=0$. Furthermore we have the following theorem:

If $L_1C_a=L_2C_b$ *then* $L_1=L_2$ *and* $C_a=C_b$.

For the singular manifolds of L_1C_a and L_2C_b must be identical. Since L_1 and L_2 are regular this implies that $C_a=C_b$ and hence $L_1=L_2$. As a consequence we see that the transformations LC_a form a fifteen parameter manifold, hence they contain all the required transformations sufficiently near to identity.

LETTERS TO THE EDITOR

Potential Gradients in Direct-Current Metal Arcs Determined from Stark Effect Studies

A recent survey of the theory of operation of direct-current arcs in air between low melting point metal electrodes indicates a rather wide-spread adherence to the belief that the electron supply at the cathode is furnished by some sort of field current emission mechanism. In support of this view and adding to the confusion already existing in the field, there is quoted a conclusion drawn by Nagaoka and Suguira in their paper on the Stark effect broadening of metal lines in arcs.[1] This conclusion is that from the observed broadening of lines, one can infer the existence of electrical field gradients of hundreds of thousands of volts per cm in the arc and especially near the cathode. In quoting these conclusions in recent years, workers on the mechanism of arc discharge fail to note that the work of Nagaoka and Suguira was done in the early days of Stark effect theory (1924), so that the early interpretations of their results require restatement in the light of present day knowledge. Failure to note these changes leads to obviously contradictory and absurd conclusions. No doubt exists that the phenomena observed by Nagaoka and Suguira and interpreted by them as a Stark effect is actually a Stark effect. Symmetrical broadening is observed in just those lines where the first-order Stark effect would be expected while similar conclusions apply to the unsymmetrical broadening ascribable to the second-order Stark effect.

The difficulty introduced by the early conclusions of Nagaoka and Suguira does not lie in their ascribing the broadening to a Stark effect. The difficulty lies only in their considering the electrical fields producing the Stark effects to be due to *linear potential gradients* along the arc column amounting in some cases near the cathode to hundreds of kv per cm. Such gradients while perhaps welcomed by adherents to a field emission theory of the arc mechanism are completely at variance with the other data. In many cases observed by Nagaoka the broadening of the lines extends nearly along the whole length of the arc, so that well in the center of the arc in the first-order broadening the fields calculated are in the tens of kv per cm. The existence of such gradients in the arc is completely negatived by probe measurements of Nagaoka and Suguira and many others in these and similar arcs. Again an integration of the measured gradients over the length of their arcs would lead to potentials across the arcs hundreds of times greater than the applied potentials.

It is obvious that the explanation of this apparent discrepancy lies in the mistake of ascribing the Stark effect to *linear potential gradients down the arc*. The absence of any structure in the broadening of the lines indicates at once the absence of any such clear cut field gradients. The fields responsible for the type of Stark broadening observed can today be entirely ascribed to the ionic force fields existing in the intensely ionized plasma of the arcs. The fields of 180 kv/cm correspond to an ion density of about 2 percent. The variations in broadening down the arc length observed by Nagaoka and Suguira represent obvious and expected changes in ion density along the arc path. It is possible that valuable data as to the ion densities in arcs could be drawn from such observations. A similar explanation was invoked by Lawrence and Dunnington[2] in their explanation of the broadening of the Mg, Cd and Zn lines in sparks observed 10^{-7} second after breakdown. In this case the fields were 10^6 volts/cm and the density of the ionization was estimated as of the order of one-third of the molecules present.

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April 17, 1936.

[1] Nagaoka and Suguira, Jap. J. Physics **3**, 45 (1924).
[2] Lawrence and Dunnington, Phys. Rev. **35**, 405 (1930).

Note on δ Quartz

In a recent issue of this journal[1] Harold Osterberg announced the discovery of a new form of crystalline quartz, called δ quartz, which he found to be not piezoelectric at temperatures below 89.6°K. We desire to call attention to papers by L. Balamuth[2] and F. Rose[3] in which these writers describe the composite piezoelectric oscillator method for measuring the elastic constants of solids at low temperatures. It is there stated that *X*- and *Y*-cut quartz cylinders can be piezoelectrically excited, respectively, to longitudinal and torsional vibration at a temperature as low as 78°K.

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F. ROSE
S. L. QUIMBY

Columbia University,
April 8, 1936.

[1] Osterberg, Phys. Rev. **49**, 552 (1936).
[2] Balamuth, Phys. Rev. **45**, 715 (1934).
[3] Rose, Phys. Rev. **49**, 50 (1936).

An Acknowledgment

Both L. H. Thomas of Ohio State University and H. P. Robertson of Princeton have drawn our attention to a paper by E. Cunningham[1] in which the author derives the transformations for the components of **E** and **H** under an inversion as given in our recent paper.[2] Cunningham, however, does not seem to have realized that the inversion transformation represents constant relative acceleration, nor does he discuss the force equation. We regret that we were unaware of Cunningham's work at the time we sent our paper to the *Physical Review*.

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N. I. ADAMS, JR.

Yale University,
New Haven, Connecticut,
April 13, 1936.

[1] Cunningham, Proc. London Math. Soc. **8**, 77 (1910).
[2] Page and Adams, Jr., Phys. Rev. **49**, 467 (1936).

Enrichment of Nitrogen in the Isotope N^{15}

In a previous letter[1] we described briefly the production and analysis of samples of methane which were enriched in the carbon isotope, C^{13}, by diffusion in a Hertz apparatus. Further diffusions with methane have given a considerably greater enrichment than that reported. Two samples showed an intensity ratio of 3.3 to 1 for the bands due to $C^{12}C^{12}$ and $C^{12}C^{13}$, corresponding to an abundance of 13.1 atomic percent for C^{13}. The head due to $C^{13}C^{13}$ could also be measured on these plates,[2] and its intensity was consistent with that of $C^{12}C^{13}$. This methane has been used by one of us to photograph the $C^{13}N^{14}$ bands under high dispersion, and from these a value for the mass ratio of the carbon isotopes has been obtained.[3]

The method has now been applied to nitrogen gas, with satisfactory results. Abundance measurements were made by observations on the isotope heads[4] accompanying the 1,0 and 2,0 bands of the second positive system of N_2. According to Urey and Murphy,[5] N^{15} is present in ordinary nitrogen to one part in 350, so that these heads due to $N^{14}N^{15}$ should have an intensity of 1/175 that of the main heads due to $N^{14}N^{14}$. A sample of 300 cc of nitrogen ($p=6$ mm) from the first diffusion gave an intensity ratio of 1/16.5. This means an abundance of 3 atomic percent of N^{15}, an enrichment by a factor of slightly greater than 10. With this gas it should be possible to measure the bands due to $C^{12}N^{15}$, and so to obtain an accurate value of the mass ratio of the nitrogen isotopes.

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April 9, 1936.

[1] Wooldridge and Jenkins, Phys. Rev. **49**, 404 (1936).
[2] Due to an error in the reproduction of the figure in our previous letter, the triple dot designating this head was considerably displaced. The other two heads were correctly marked, and the three heads, due to $C^{12}C^{12}$, $C^{12}C^{13}$, and $C^{13}C^{13}$, should to the eye appear equally spaced.
[3] Jenkins and Wooldridge, paper given at the Washington meeting of the American Physical Society, April 30, 1936.
[4] G. Herzberg, Zeits. f. physik. Chemie **B9**, 43 (1930).
[5] H. C. Urey and G. M. Murphy, Phys. Rev. **41**, 141 (1932).

A Spectrographic Method of Measuring Carbon Dioxide Concentration

Chemical methods of estimating the CO_2 concentration in a mixture of gases, such as in air, require very accurate temperature control and are slow in action. For example, in a continuous flow method[1] used in this laboratory the temperature of the electrolytic cell must be held constant to better than 0.01°C and about 30 minutes are required to obtain an individual reading. The physical method of observing the heat conductivity of the gas also requires an extremely accurate temperature control. This latter method measures a physical property of *all gases*, thus when used it is necessary to know the other gases present and make the proper corrections for them. Recently (November 21, 1935) a spectrographic method was tested in this laboratory and found to be very successful.

This method makes use of the high opacity of CO_2 gas to radiation in the region of one of its fundamental absorption bands. The spectral region used is a band from 4.2 to 4.3μ, so chosen because water vapor and practically *all* of the other gases or vapors commonly found in air are transparent to this radiation. Radiation of this wavelength is isolated from a suitable source (Nernst filament) by means of an infrared spectrograph and allowed to fall upon a vacuum thermocouple after passing through a known optical path length of air contained in an absorption tube. The apparatus is calibrated by filling the absorption tube with air free from CO_2 then with air of a known concentration of CO_2 and the galvanometer deflections observed. For the range of concentrations from zero to 0.10 percent CO_2 an 86 cm optical path length is used. With this arrangement the sensitivity of the apparatus is such that a one-millimeter deflection represents one-ten thousandth of one percent CO_2. Shorter path lengths enable the measurement of greater concentrations. Two millimeters of pure CO_2 at N.T.P. transmit only 22 percent of the radiation 4.2 to 4.3μ.

The particular advantages of this spectrographic method are: (1) The sensitivity is as great as that of the best chemical method, (2) it gives instantaneous measurements (galvanometer response 5 seconds), (3) the measurements are independent of the humidity of the air and also independent of the presence of practically all of the other gases or vapors commonly found in air, (4) for ordinary room temperatures and pressures the apparatus has very small temperature and pressure corrections (3°C or 7 mm pressure change cause about 1 percent change in sensitivity), and (5) it can be recalibrated in a few seconds, which enables the use of full sensitivity. The same arrangement can be used to observe small concentrations of other gases by selecting radiation of appropriate wave-lengths.

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Division of Radiation and Organisms,
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Washington, D. C.,
April 15, 1936.

[1] E. C. White, J. Am. Chem. Soc. **50**, 2148 (1928).

Focusing Effect of Double Crystal Spectrometer

The focusing effect of the double crystal spectrometer in the antiparallel position recently discussed by Parratt[1] was developed in detail by the author[2] and later used by A. H. Barnes.[3]

If $\Delta\theta$ is the difference in Bragg angle between the x-ray which passes through the axis of the second crystal and any other x-ray, then the two rays will intersect at a distance from the axis equal to $\sin\Delta\theta/\sin 3\Delta\theta$ (approximately one-third) the distance from the target to the axis. In addition to the focus "fixed in space" there is also a focus "moving with the second crystal" which is three times as far from the axis, i.e., at a distance equal to the x-ray path from the target to the axis.

The advantage of placing slits or ionization chamber windows at these foci was pointed out by the author.

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The Brace Laboratory of Physics,
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Lincoln, Nebraska,
April 18, 1936.

[1] Parratt, Rev. Sci. Inst. **6**, 389 (1935).
[2] R. C. Spencer, Phys. Rev. **38**, 620 (1931).
[3] A. H. Barnes, Phys. Rev. **44**, 141 (1933).